

Supporting Information

for

Study of tribenzo[*b,d,f*]azepine as donor in D-A photocatalysts.

Katy Medrano-Urbe¹, Jorge Humbrías-Martín¹, and Luca Dell'Amico¹.

Address: ¹Department of Chemical Sciences, University of Padova, Via Francesco Marzolo 1, 35131, Padova (Italy).

Contents

A. General Information	3
B. Experimental setup for light irradiation Reaction setup with Kessil LED PR160L	5
C. Synthesis of the sulfur-based acceptors and tribenzo[<i>b,d,f</i>]azepine	6
2-bromodibenzo[<i>b,d</i>]thiophene (17)	6
2-bromodibenzo[<i>b,d</i>]thiophene 5,5-dioxide (18)	6
(4-bromophenyl)(phenyl)sulfane (19).....	6
1-bromo-4-(phenylsulfonyl)benzene (20)	6
2-bromo-9,9-dimethyl-9 <i>H</i> -thioxanthene (21).....	6
2-bromo-9,9-dimethyl-9 <i>H</i> -thioxanthene (22).....	7
2-bromo-9,9-dimethyl-9 <i>H</i> -thioxanthene 10,10-dioxide (23)	7
tribenzo[<i>b,d,f</i>]azepine (a)	7
D. Synthesis of the D-A photocatalysts	8
General procedure A	8
9-(4-(phenylsulfonyl)phenyl)-9 <i>H</i> -tribenzo[<i>b,d,f</i>]azepine (4a).....	8
2-(9 <i>H</i> -tribenzo[<i>b,d,f</i>]azepin-9-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5a).....	8
9,9-dimethyl-2-(9 <i>H</i> -tribenzo[<i>b,d,f</i>]azepin-9-yl)-9 <i>H</i> -thioxanthene 10,10-dioxide (6a)	9
2-(5 <i>H</i> -dibenzo[<i>b,f</i>]azepin-5-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5b)	9
2-(9 <i>H</i> -carbazol-9-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5c).....	9
2-(diphenylamino)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5d).....	10
2-(10 <i>H</i> -phenoxazin-10-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5e).....	10
E. Photoredox properties Luminescence quantum yield measurements	11
Photoredox properties summary	11

9-(4-(phenylsulfonyl)phenyl)-9 <i>H</i> -tribenzo[<i>b,d,f</i>]azepine (4a).....	13
2-(9 <i>H</i> -tribenzo[<i>b,d,f</i>]azepin-9-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5a).....	16
9,9-dimethyl-2-(9 <i>H</i> -tribenzo[<i>b,d,f</i>]azepin-9-yl)-9 <i>H</i> -thioxanthene 10,10-dioxide (6a)	19
2-(5 <i>H</i> -dibenzo[<i>b,f</i>]azepin-5-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5b).....	22
2-(9 <i>H</i> -carbazol-9-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5c).....	25
2-(diphenylamino)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5d).....	28
2-(10 <i>H</i> -phenoxazin-10-yl)dibenzo[<i>b,d</i>]thiophene 5,5-dioxide (5e).....	31
F. Cyclic voltammetries of donors and acceptors	34
G. Evaluation of the photoredox performances	36
Oxidative quenching cycle study	36
General Procedure B	36
General Procedure C.....	37
Reductive quenching cycle study	38
General Procedure D.....	38
General Procedure E.....	39
H. Theoretical studies	40
I. References	48
J. NMR spectra	49

A. General Information

All reactions were carried out in anhydrous solvents purchased from commercial suppliers over molecular sieves in a sealed bottle which were used without further purification. Chemicals were purchased from commercial sources (Sigma–Aldrich, Fluorochem or TCI) and used without further purification. Organic solvents were purchased from Sigma–Aldrich. Reactions were monitored by thin- layer chromatography on silica gel 60F254, and/or by NMR spectroscopy.

NMR spectra were collected on a Bruker 400 Avance III HD spectrometer equipped with a BBI-z grad probehead, at the denoted spectrometer frequency given in MHz for the specified nucleus. Reported coupling constants and chemical shifts were based on a first order analysis. The internal reference for ^1H NMR was the residual peak of CDCl_3 (7.26 ppm). The internal reference for ^{13}C NMR was the residual peak of CDCl_3 (77.16 ppm). All coupling constants (J) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, ddd= double of doublets of doublets, t = triplet, dt = double triplet, q = quadruplet, m = multiplet, br = broad.

Thin-layer chromatography (TLC) analysis was performed on pre-coated Merck TLC plates (silica gel 60G F254, 0.25 mm). Chromatographic purification of the products was accomplished using flash chromatography on silica gel (SiO_2 , 0.04-0.0063 mm) purchased from Sigma-Aldrich, with the indicated solvent system according to the standard techniques, or with pre-coated Merck preparative TLC plates (silica gel 60G F254, 20x20 cm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Steady-state absorption spectroscopy studies were performed at room temperature on a Varian Cary 50 UV-vis; 10 mm path length Hellma Analytics 100 QS quartz cuvettes were used.

Steady-state emission spectroscopy studies were performed at room temperature on a Varian Cary Eclipse Fluorescence spectrophotometer; 10 mm path length Hellma Analytics 117.100F QS quartz cuvettes were used.

Excited-state lifetimes measurements were performed at room temperature on a FLS1000 UV/Vis/NIR photoluminescence spectrometer (Edinburgh Instruments) at the PanLab facility of the Department of Chemical Sciences, University of Padova, funded by the MIUR- "Dipartimenti di Eccellenza" grant NEXUS. The instrument was coupled with a high-speed detector with amplifier, operating in the spectral range: 230-850 nm and with a response time width.

The electrochemical characterizations were carried out in acetonitrile (MeCN)/0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) at room temperature, on an BASi EC Epsilon potentiostat-galvanostat in a glass cell. All the cyclic voltammograms were recorded with a scan rate of 0.1 V/s. A typical three-electrode cell was employed, which was composed of a glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and an Ag/AgCl electrode as reference electrode. The glass electrochemical cell was kept closed with a stopper annexed to the potentiostat. Oxygen was removed by purging the solvent with high-purity Nitrogen (N_2), introduced from a line into the cell by means of a glass pipe. The potential of ferrocenium/ferrocene (Fc^+/Fc) couple was used as internal reference system to calibrate the potentiostat. All the results were subsequently converted in V vs SCE, in agreement with the value reported in literature [$E_{1/2}(\text{Fc}^+/\text{Fc}) = +0.395$ V vs SCE].

The IR compensation implemented within the potentiostat was used, and every effort was made throughout the experiments to minimize the resistance of the solution. The full electrochemical reversibility of the voltammetric wave of ferrocene was taken as an indicator of the absence of uncompensated resistance effects. The GC electrode was polished before any measurement with diamond paste, carefully rinsed with de-ionized water, ethanol, acetone and ultrasonically rinsed with a methanol/ethanol/acetone 1:1:1 (v/v) mixture for 5 minutes. After each series of CV experiments, the electrochemical cell was carefully rinsed with ethanol, acetone and de- ionized water; afterwards, the cell and the magnetic stirrer were sonicated for 5-10 min with acetone.

High-resolution mass spectrometry (HRMS) analyses were performed on MicroTOF-Q Bruker (ESI) and a GC Thermo Scientific Trace 1300 GC unit coupled to an APPI MasCom source mounted on a Thermo Scientific Exactive Plus EMR mass unit (Orbitrap FT-HRMS analyzer) or on a Xevo G2-XS QToF.

The Kessil lamps PR160L (50W) were purchased from Kessil webpage: https://kessil.com/products/science_PR160L.php

B. Experimental setup for light irradiation Reaction setup with Kessil LED PR160L

Figure S1 shows the general setup of a batch reaction performed under Kessil LED PR160L light irradiation (400 nm). The reaction mixture is placed at a fixed distance (about 3 cm) from the light source and stirred vigorously. A maximum of three reaction vessels were irradiated at the same time, following the lines of homogeneous irradiance provided by the producer. To maintain a stable reaction temperature, one fan was placed above the irradiated vials. All the reactions were carried out using 100% intensity.

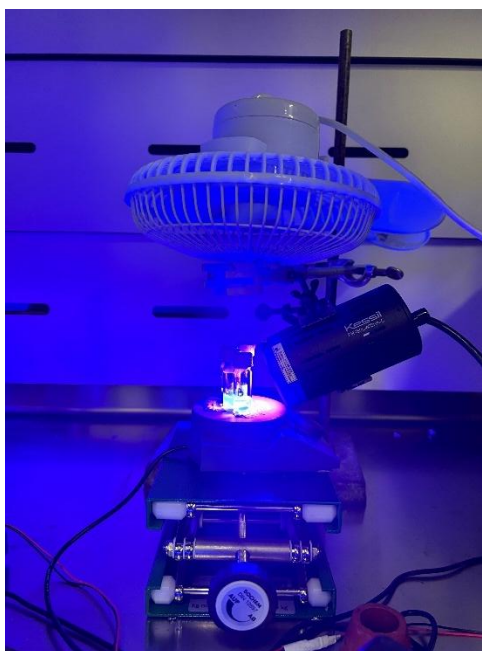
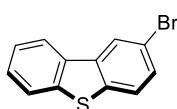


Figure S1: Reaction setup using Kessil lights

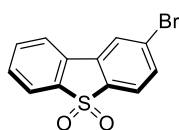
C. Synthesis of the sulfur-based acceptors and tribenzo[*b,d,f*]azepine.

2-bromodibenzo[*b,d*]thiophene (17)



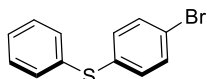
2-bromodibenzo[*b,d*]thiophene **17** was synthesized following a reported procedure.¹ The spectral data matched with those reported in the literature.² **¹H NMR (400 MHz, CDCl₃)** δ 8.30 – 8.26 (m, 1H), 8.10 (ddd, *J* = 9.1, 6.3, 3.0 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.72 (dd, *J* = 8.6, 6.4 Hz, 1H), 7.57 (ddd, *J* = 8.5, 3.4, 1.8 Hz, 1H), 7.52 – 7.48 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 140.01, 138.09, 137.34, 134.43, 129.57, 127.38, 124.67, 124.51, 124.09, 122.89, 121.77, 118.33.

2-bromodibenzo[*b,d*]thiophene 5,5-dioxide (18)



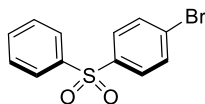
2-bromodibenzo[*b,d*]thiophene 5,5-dioxide **18** was synthesized following a reported procedure.³ The spectral data matched with those reported in the literature.⁴ **¹H NMR (400 MHz, CDCl₃)** δ 7.94 (s, 1H), 7.89 – 7.81 (m, 1H), 7.81 – 7.72 (m, 1H), 7.71 – 7.63 (m, 3H), 7.56 (dtd, *J* = 16.0, 7.5, 1.0 Hz, 1H). **¹³C NMR (400 MHz, CDCl₃)** δ 138.1, 136.5, 134.1, 133.6, 133.3, 131.1, 130.3, 128.7, 125.0, 123.5, 122.4, 121.8.

(4-bromophenyl)(phenyl)sulfane (19)



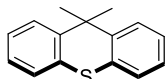
(4-bromophenyl)(phenyl)sulfane **19** was synthesized following a reported procedure.¹ The spectral data matched with those reported in the literature.⁵ **¹H NMR (400 MHz, CDCl₃)** δ 7.48 – 7.39 (m, 2H), 7.39 – 7.25 (m, 5H), 7.22 – 7.14 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 135.63, 134.95, 132.35, 132.21, 131.68, 129.50, 127.69, 120.99.

1-bromo-4-(phenylsulfonyl)benzene (20)



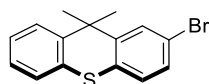
1-bromo-4-(phenylsulfonyl)benzene **20** was synthesized following a reported procedure.³ The spectral data matched with those reported in the literature.⁶ **¹H NMR (400 MHz, CDCl₃)** δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 141.18, 140.71, 133.47, 132.62, 129.43, 129.22, 128.48, 127.67.

2-bromo-9,9-dimethyl-9*H*-thioxanthene (21)



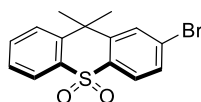
2-bromo-9,9-dimethyl-9*H*-thioxanthene **21** was synthesized following a reported procedure.⁷ The chemical shifts obtained matched with those reported in the literature.⁷ **¹H NMR (400 MHz, CDCl₃)** δ 7.60 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.33 (td, *J* = 7.6, 1.5 Hz, 2H), 7.26 (td, *J* = 7.5, 1.4 Hz, 2H), 1.76 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 142.35, 132.96, 127.32, 126.69, 126.13, 124.72, 40.37, 25.20.

2-bromo-9,9-dimethyl-9*H*-thioxanthene (22)



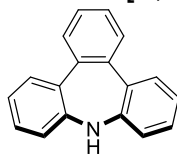
2-bromo-9,9-dimethyl-9*H*-thioxanthene 10,10-dioxide **22** was synthesized following a reported procedure.⁸ The compound was obtained in quantitative yield and used without further purification for the next step reaction. **¹H NMR (400 MHz, CDCl₃)** δ 7.65 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.54 (ddd, *J* = 7.6, 5.5, 1.4 Hz, 1H), 7.46 (ddd, *J* = 7.5, 5.5, 1.5 Hz, 1H), 7.38 – 7.26 (m, 3H), 7.22 (tdd, *J* = 7.4, 5.1, 1.4 Hz, 1H), 1.69 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 144.52, 141.61, 132.35, 132.17, 128.94, 128.52, 127.94, 127.23, 126.86, 126.25, 126.01, 124.73, 120.49, 41.20, 24.76.

2-bromo-9,9-dimethyl-9*H*-thioxanthene 10,10-dioxide (23)



2-bromo-9,9-dimethyl-9*H*-thioxanthene 10,10-dioxide **23** was synthesized following a reported procedure.³ Purification by FC over silica gel (Hexane/AcOEt 70/30) afforded **23** in 68% yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.20 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.07 (t, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 6.3, 1.7 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.54 (tt, *J* = 7.6, 2.8 Hz, 1H), 1.91 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.91, 145.22, 136.54, 135.92, 133.11, 130.75, 129.08, 127.84, 127.72, 125.97, 125.66, 124.37, 40.13, 30.37.

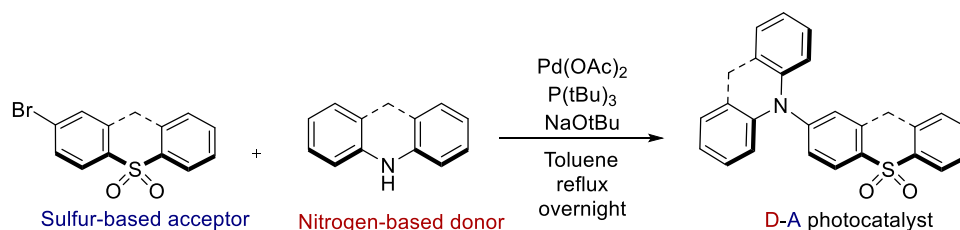
tribenzo[b,d,f]azepine (a)



Tribenzo[b,d,f]azepine (**a**) was synthesized following a reported procedure.⁹ The spectral data matched with those reported in the literature. **¹H NMR (400 MHz, CDCl₃)** δ 7.53 – 7.47 (m, 4H), 7.44 (dt, *J* = 5.8, 3.5 Hz, 2H), 7.23 (ddd, *J* = 9.3, 6.9, 3.1 Hz, 2H), 7.13 (td, *J* = 7.6, 1.4 Hz, 2H), 6.90 (dd, *J* = 7.8, 1.3 Hz, 2H), 5.20 (s, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 151.10, 139.49, 132.79, 130.30, 130.24, 128.59, 127.89, 124.26, 119.87.

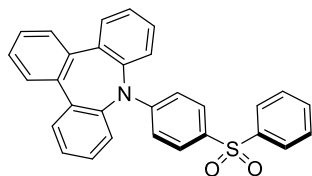
D. Synthesis of the D-A photocatalysts

General procedure A



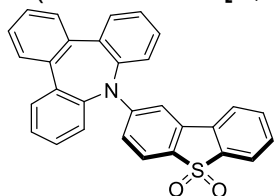
The procedure was modified from the one reported in the literature.¹⁰ A 100 ml two-neck flask with a condenser and a Teflon-coated magnetic stir bar was charged with the sulfur-based acceptor (1 equiv), nitrogen-based donor (1.2-2.0 equiv), Pd(OAc)₂ (0.04 equiv), and NaOtBu (1.5-2.0 equiv). The reaction mixture was purged with Argon for 10 minutes. Then, toluene (0.025 M) was added, followed by the addition of P(tBu)₃ (0.08 equiv), and the reaction was purged with Argon 10 more minutes. The reaction was heated until reflux (120°C, approx.) for 12 h. Upon completion, the reaction mixture was cooled at room temperature and poured into water and extracted with toluene three times. The combined organic layers were washed with water and dried over Na₂SO₄. After filtration and solvent evaporation purified by flash column chromatography (FC) over silica gel to furnish the target product.

9-(4-(phenylsulfonyl)phenyl)-9H-tribenzo[*b,d,f*]azepine (**4a**)



Synthesized following the general procedure starting from 1-bromo-4-(phenylsulfonyl)benzene (38.3 mg, 0.128 mmol, 1 equiv), Tribenzo[*b,d,f*]azepine (46.7 mg, 0.192 mmol, 1.2 equiv), Pd(OAc)₂ (1.12 mg, 0.005 mmol, 0.04 equiv), NaOtBu (18 mg, 0.193 mmol, 1.5 equiv) and P(tBu)₃ (2.6 ml, 0.010 mmol, 0.08 equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 9:1 as eluent. Compound **4a** was obtained in 36% yield. **¹H NMR (400 MHz, CDCl₃)** δ 7.81 (dt, *J* = 7.1, 1.5 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.59 (dd, *J* = 5.8, 3.5 Hz, 2H), 7.53 – 7.37 (m, 13H), 6.55 – 6.50 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 151.31, 144.52, 143.14, 138.64, 137.02, 132.50, 131.27, 129.61, 129.44, 129.31, 129.14, 128.87, 128.34, 128.28, 128.06, 127.21, 111.74. **HRMS (ESI+):** *m/z* calcd. for C₃₀H₂₂NO₂S [MH]⁺: 460.1366. Found: 460.1364.

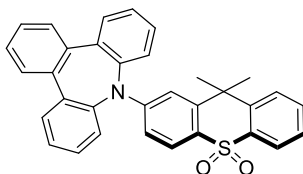
2-(9H-tribenzo[*b,d,f*]azepin-9-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**5a**)



Synthesized following the general procedure starting from 2-bromodibenzo[*b,d*]thiophene 5,5-dioxide (160 mg, 0.544 mmol, 1 equiv), Tribenzo[*b,d,f*]azepine (158 mg, 0.652 mmol, 1.2 equiv), Pd(OAc)₂ (4 mg, 0.017 mmol, 0.04 equiv), NaOtBu (62 mg, 0.645 mmol, 1.5 equiv) and P(tBu)₃ (8.5 ml, 0.034 mmol, 0.08 equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 9:1 as eluent. Compound **5a** was obtained in 45% yield. **¹H NMR (400 MHz, CDCl₃)** δ 7.71 (ddt, *J* = 11.4, 7.4, 1.1 Hz, 3H), 7.63 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.56 – 7.35 (m, 12H), 6.76 (d, *J* = 2.2 Hz, 1H), 6.53 (dd, *J* = 8.7, 2.2 Hz, 1H). **¹³C NMR (101 MHz, CDCl₃)** 152.49, 144.55, 139.23, 138.86, 136.95, 133.47, 133.33, 132.00, 131.48, 130.21, 129.71, 129.67, 128.65, 128.57, 128.37,

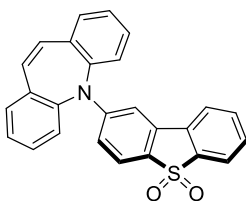
125.94, 123.32, 121.91, 121.50, 113.14, 103.58. **HRMS (ESI+)**: m/z calcd. for C₃₀H₂₀NO₂S [MH]⁺ : 458.1209. Found: 458.1214.

9,9-dimethyl-2-(9H-tribenzo[*b,d,f*]azepin-9-yl)-9H-thioxanthene 10,10-dioxide (6a)



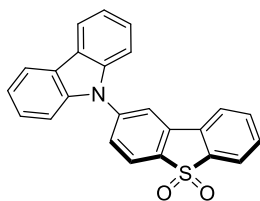
Synthesized following the general procedure starting from 2-bromo-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (83.1 mg, 0.246 mmol, 1 equiv), Tribenzo[*b,d,f*]azepine (72 mg, 0.295 mmol, 1.2 equiv), Pd(OAc)₂ (2.2 mg, 0.001 mmol, 0.04 equiv), NaOtBu (35 mg, 0.369 mmol, 1.5 equiv) and P(*t*Bu)₃ (5 ml, 0.002 mmol, 0.08 Equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 9:1 as eluent. Compound **6a** was obtained in 68% yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.08 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.72 (dd, *J* = 11.0, 8.2 Hz, 3H), 7.63 – 7.56 (m, 3H), 7.51 – 7.43 (m, 7H), 7.44 – 7.36 (m, 3H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.53 (dd, *J* = 8.8, 2.3 Hz, 1H), 1.54 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 150.95, 147.13, 145.74, 144.59, 138.70, 137.59, 136.91, 132.19, 131.18, 129.41, 129.33, 128.22, 128.13, 127.17, 125.65, 125.36, 124.76, 123.72, 116.35, 110.38, 107.91, 39.16, 31.04. **HRMS (ESI+)**: m/z calcd. for C₃₃H₂₆NO₂S [MH]⁺ : 500.1679. Found: 500.1673.

2-(5H-dibenzo[*b,f*]azepin-5-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (5b)



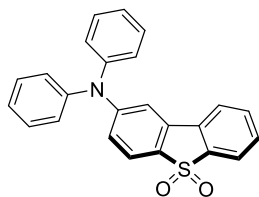
Synthesized following the general procedure starting from 2-bromo-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (350 mg, 1.18 mmol, 1 equiv), and commercial 5H-Dibenzo[*b,f*]azepine (342 mg, 1.77 mmol, 1.5 equiv), Pd(OAc)₂ (10.6 mg, 0.047 mmol, 0.04 equiv), NaOtBu (170 mg, 1.77 mmol, 1.5 equiv) and P(*t*Bu)₃ (23 ml, 0.019 mmol, 0.08 Equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 75:25 as eluent. Compound **5b** was obtained in 54% yield. **¹H NMR (400 MHz, CDCl₃)** δ 7.73 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.57 (td, *J* = 7.4, 6.9, 1.7 Hz, 2H), 7.51 (dt, *J* = 7.7, 1.6 Hz, 4H), 7.48 – 7.39 (m, 5H), 7.36 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.88 (s, 2H), 6.53 (d, *J* = 2.2 Hz, 1H), 6.32 (dd, *J* = 8.7, 2.2 Hz, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 154.34, 142.22, 139.33, 136.44, 134.22, 133.74, 132.10, 131.38, 131.18, 130.87, 130.72, 130.20, 128.67, 126.97, 123.62, 122.44, 121.91, 113.78, 104.30. **HRMS (ESI+)**: m/z calcd. for C₂₆H₁₈NO₂S [MH]⁺ : 408.1053. Found: 408.1050.

2-(9H-carbazol-9-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (5c)



Synthesized following the general procedure starting from 2-bromo-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (350 mg, 1.18 mmol, 1 equiv), and commercial carbazole (396 mg, 2.37 mmol, 2 equiv), Pd(OAc)₂ (10.6 mg, 0.047 mmol, 0.04 equiv), NaOtBu (170 mg, 1.77 mmol, 1.5 equiv) and P(*t*Bu)₃ (23 ml, 0.019 mmol, 0.08 Equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 7:3 as eluent. Compound **5c** was obtained in 64 % yield. **¹H NMR (400 MHz, CDCl₃)** δ 8.20-8.14 (m, 2H), 8.07 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.02 (d, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.68 (tt, *J* = 7.6, 1.4 Hz, 1H), 7.61 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.36 (ddt, *J* = 7.8, 5.4, 1.8 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 143.53, 140.29, 138.46, 135.92, 134.22, 131.22, 130.94, 128.61, 126.63, 124.13, 122.59, 122.02, 121.15, 120.79, 119.92, 109.68. **HRMS (ESI+)**: m/z calcd. for C₂₄H₁₆NO₂S [MH]⁺ : 382.0896. Found: 382.0899.

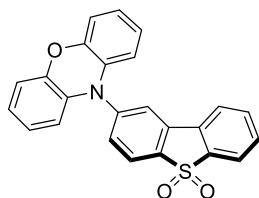
2-(diphenylamino)dibenzo[*b,d*]thiophene 5,5-dioxide (**5d**)



Synthesized following the general procedure starting from 2-bromo-9,9-dimethyl-9*H*-thioxanthene 10,10-dioxide (443 mg, 1.5 mmol, 1 equiv), and commercial diphenylamine (305 mg, 1.8 mmol, 1.2 equiv), Pd(OAc)₂ (13.5 mg, 0.06 mmol, 0.04 equiv), NaOtBu (216 mg, 2.25 mmol, 1.5 equiv) and P(tBu)₃ (29.6 ml, 0.12 mmol, 0.08 Equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 7:3 as eluent. Compound **5d** was obtained in 55 % yield.

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.4 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 4.3 Hz, 2H), 7.52 (dq, *J* = 8.2, 4.3, 3.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 4H), 7.33 (t, *J* = 1.7 Hz, 1H), 7.20 (m, 6H), 7.05 (dt, *J* = 8.7, 1.8 Hz, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 153.40, 146.36, 138.88, 133.55, 133.50, 131.67, 130.41, 130.00, 128.78, 126.13, 125.24, 123.36, 122.07, 121.79, 121.62, 112.52. **HRMS (ESI+)**: *m/z* calcd. for C₂₄H₁₈NO₂S [MH]⁺ : 384.1053. Found: 384.1057.

2-(10*H*-phenoxazin-10-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**5e**)



Synthesized following the general procedure starting from 2-bromo-9,9-dimethyl-9*H*-thioxanthene 10,10-dioxide (350 mg, 1.18 mmol, 1 equiv), and commercial phenoxazine (434 mg, 2.37 mmol, 2 equiv), Pd(OAc)₂ (10.6 mg, 0.047 mmol, 0.04 equiv), NaOtBu (170 mg, 1.77 mmol, 1.5 equiv) and P(tBu)₃ (23 ml, 0.019 mmol, 0.08 Equiv). The reaction crude was purified by Flash column chromatography using Hexane/AcOEt 8:2 as eluent. Compound **5e** was obtained in 71 % yield.

The chemical shifts obtained matched with those reported in the literature.¹¹ **¹H NMR (400 MHz, CDCl₃)** δ 8.08 (dd, *J* = 15.6, 8.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.84 – 7.74 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.65 – 7.50 (m, 2H), 6.74 (qd, *J* = 7.9, 4.2 Hz, 4H), 6.69 – 6.58 (m, 2H), 6.02 – 5.98 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 145.75, 144.78, 144.71, 138.76, 138.00, 136.00, 134.89, 134.08, 133.96, 131.84, 131.34, 125.75, 125.18, 124.21, 123.24, 123.21, 123.07, 122.76, 116.80, 116.71, 114.26, 114.14. **HRMS (ESI+)**: *m/z* calcd. for C₂₄H₁₆NO₃S [MH]⁺ : 398.0845. Found: 398.0847.

E. Photoredox properties Luminescence quantum yield measurements.

The luminescence quantum yield measurements were performed with Anthracene 1×10^{-5} M in MeCN for compounds **5a-5d**, while for compound **5e** Fluorescein 1×10^{-5} M in MeCN was used as the standard following a literature procedure.¹² The fluorescence quantum yields were calculated according to equation:

$$\Phi_x = \Phi_{st} \times (I_x / I_{st}) \times (f_{st} / f_x) \times (\eta^2_x / \eta^2_s)$$

I is the measured integrated fluorescence emission intensity, f is the absorption factor, η is the refractive index of the solvent and Φ is the quantum yield. The index x denotes the sample and the index st denotes the standard.

Redox potential of the excited state

The oxidation potential of the excited state photocatalysts E^*_{ox} was estimated by means of the Rehm- Weller formula:

$$E^*_{ox} = E_{ox} - E_{0,0}$$

$$E^*_{red} = E_{0,0} + E_{red}$$

The oxidation potential E_{ox} and E_{red} were determined by cyclic voltammetry measurements and the excitation energy $E_{0,0}$ was determined from the intersection point between the absorption and the emission profiles.¹³

Photoredox properties summary

Acceptor analysis

PC	λ_{max} abs (nm)	λ_{max} em (nm)	$E_{0,0}$ (eV)	τ (ns)	Stokes shift (nm)	E_{ox} (V)	E^*_{ox} (V)	E_{red} (V)	E^*_{red} (V)
4a	308	389,479	3.7	$\tau_1 = 0.9$ $\tau_2 = 4.2$	81	1.57	-2.1	-2.28	1.42
5a	320	430	3.3	$\tau_1 = 1.6$ $\tau_2 = 5$	110	1.54	-1.76	-1.89	1.41
6a	292	398	3.7	$\tau_1 = 1.7$ $\tau_2 = 6$	106	1.54	-2.16	-2.4	1.3

Table S1: All potentials in V vs SCE. Measurements were performed in MeCN at room temperature.

Donor analysis

PC	λ_{max} abs (nm)	λ_{max} em (nm)	$E_{0,0}$ (eV)	τ (ns)	Stokes shift (nm)	QY (%)	E_{ox} (V)	E^*_{ox} (V)	E_{red} (V)	E^*_{red} (V)
5a	320	430	3.3	$\tau_1=1.6$ $\tau_2=5$	110	10	1.54	-1.76	-1.89	1.41
5b	312	441	3.2	0.7	129	11	1.41	-1.79	-1.86	1.34
5c	336	493	3.1	11.6	157	22	1.44	-1.66	-1.7	1.4
5d	346	525	2.9	9.1	179	35	1.23	-1.67	-1.8	1.1
5e	393	564	2.6	$\tau_1=3.3$ $\tau_2=8.7$	171	39	0.83	-1.77	-1.66	0.94

Table S2: All potentials in V vs SCE. Measurements were performed in MeCN at room temperature.

9-(4-(phenylsulfonyl)phenyl)-9H-tribenzo[*b,d,f*]azepine (**4a**)

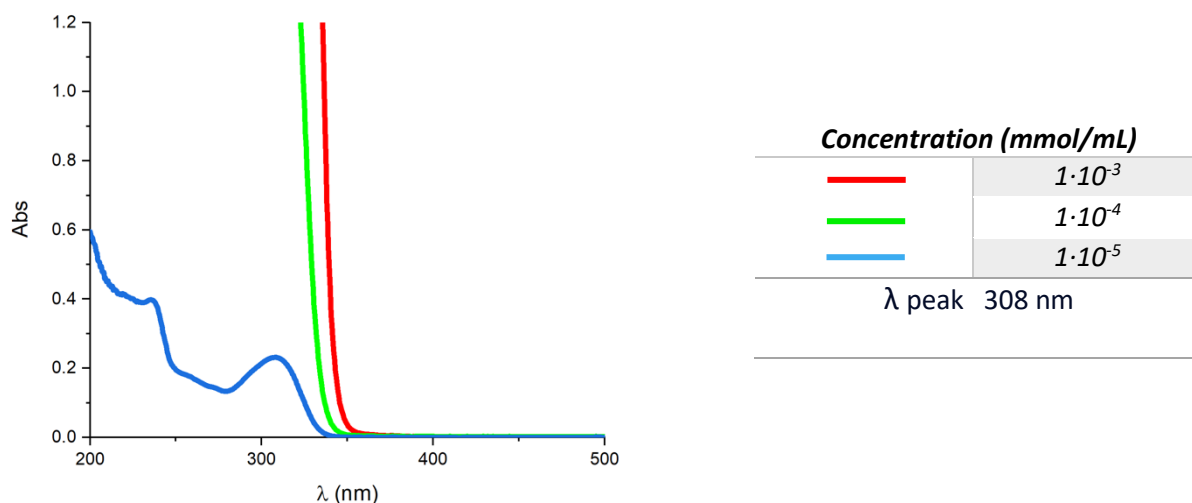
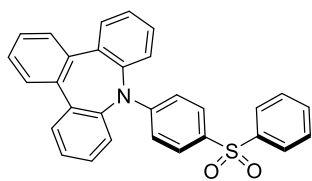


Figure S2: UV-Vis absorption of **4a** at different concentrations. $1 \cdot 10^{-3}$ M (red trace); $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

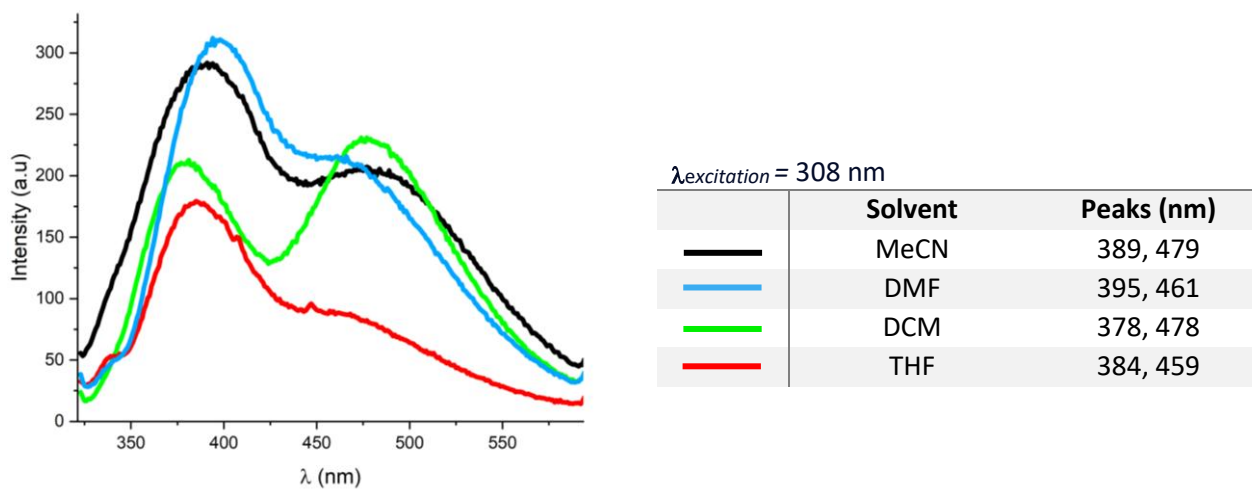


Figure S3: Normalized fluorescence emission of **4a** $1 \cdot 10^{-6}$ M in different solvents. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

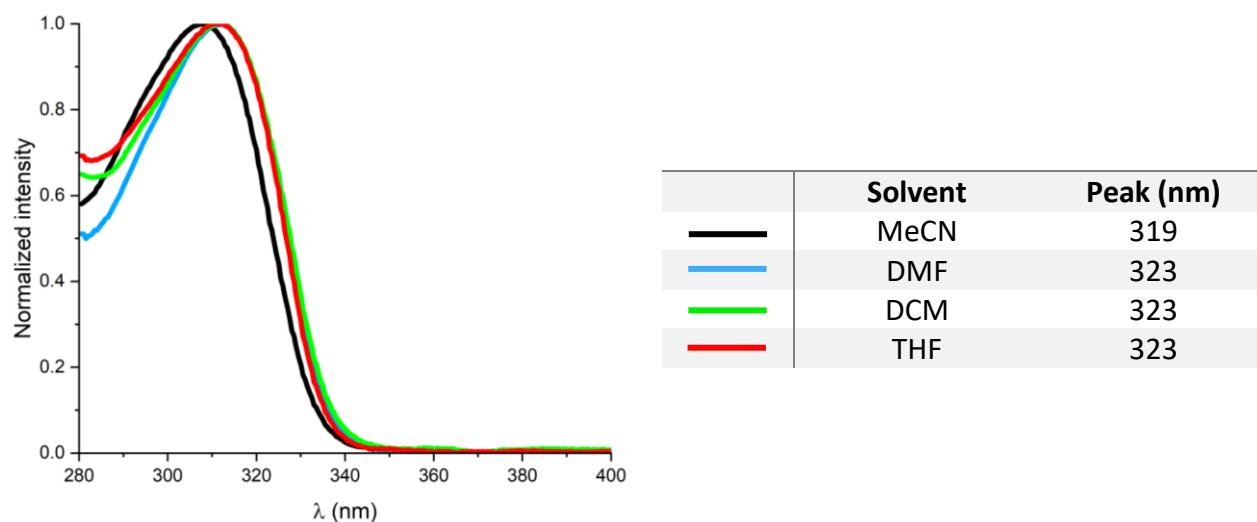


Figure S4: Normalized absorption profile of **4a** $1 \cdot 10^{-5}$ M in different solvents. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

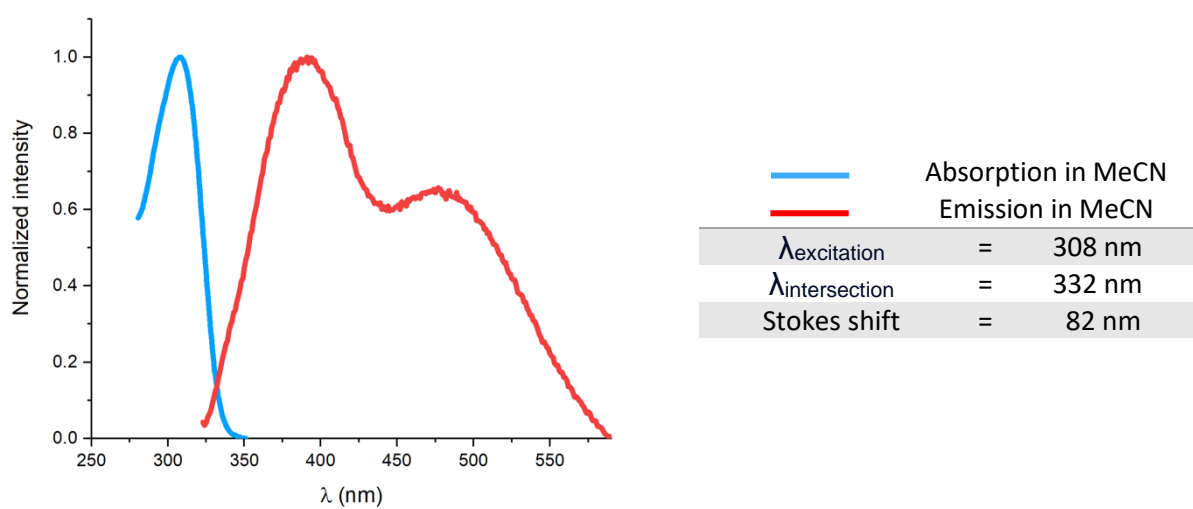


Figure S5: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **4a**.

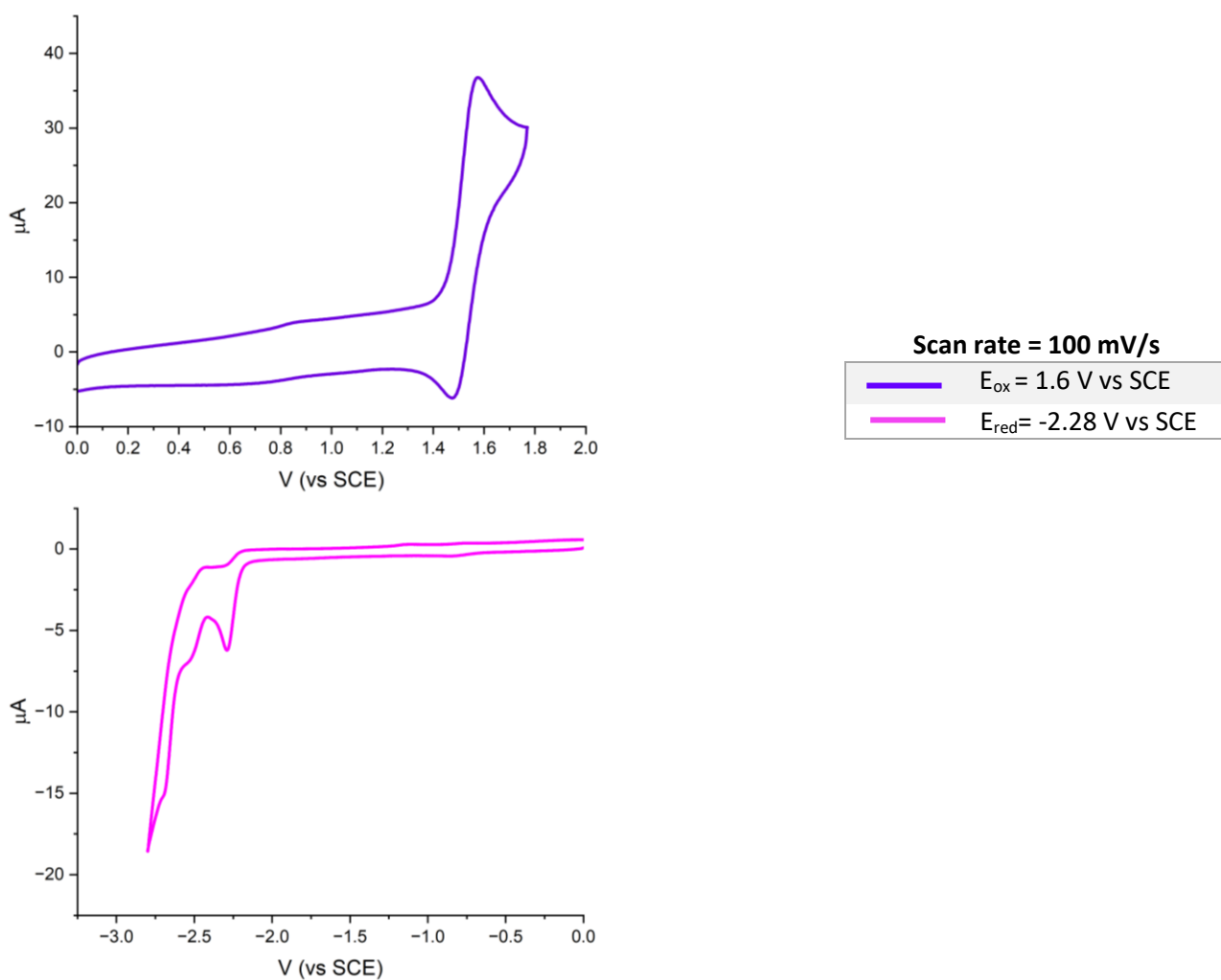


Figure S6: Cyclic voltammograms of **4a** 1×10^{-3} M. Recorded with GC as the working electrode in MeCN with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte at 0.1 V/s scan rate.

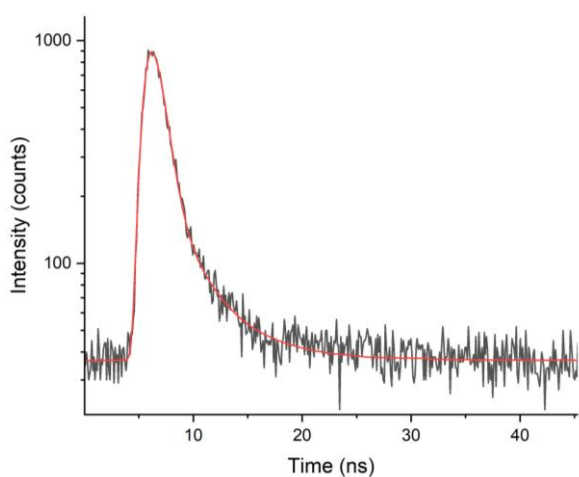


Figure S7: Time-resolved emission decay (excitation at 340 nm) of **4a** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC-SPC ($\tau = 0.9$ ns, $t = 4.2$ ns), from deconvolution and single-exponential fitting, $X^2 = 1.05$).

2-(9*H*-tribenzo[*b,d,f*]azepin-9-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**5a**)

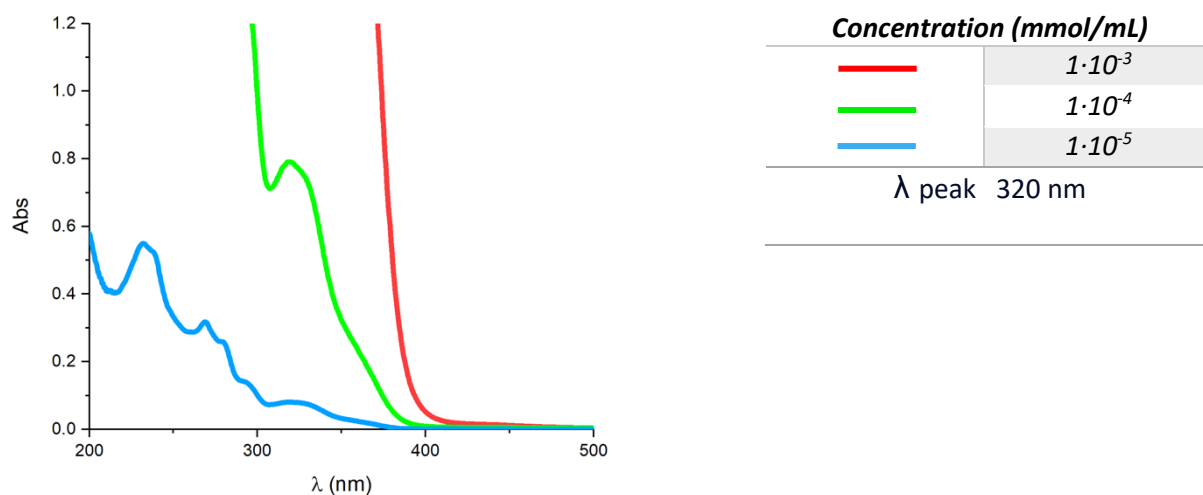
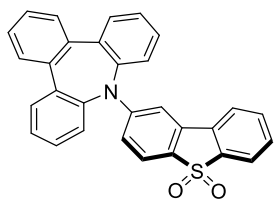


Figure S8: UV-Vis absorption of **5a** at different concentrations. $1 \cdot 10^{-3}$ M (red trace); $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

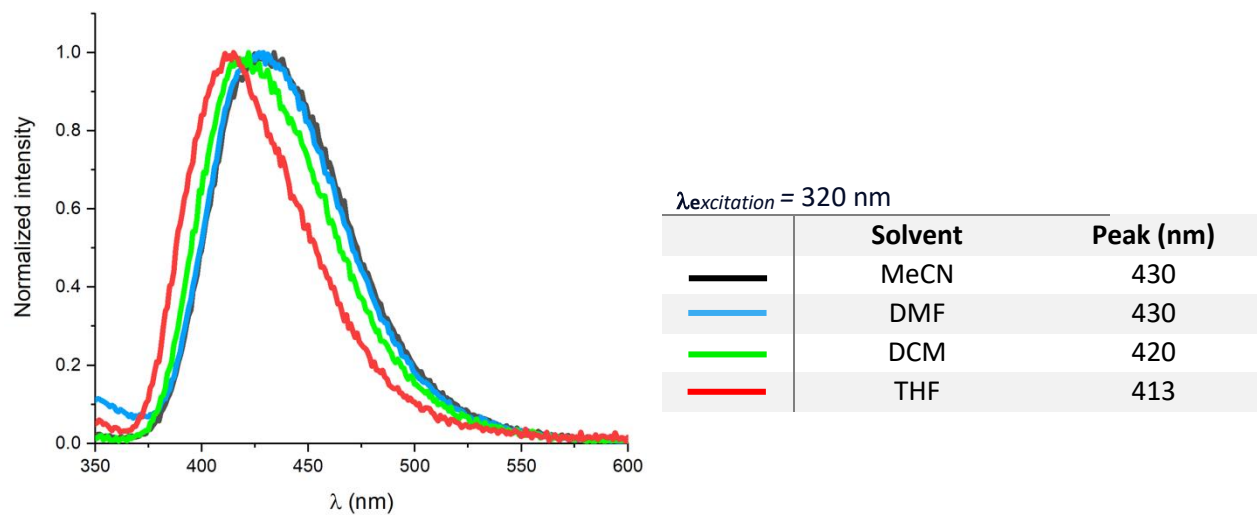


Figure S9: Normalized fluorescence emission of **5a** $1 \cdot 10^{-5}$ M in different solvents. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

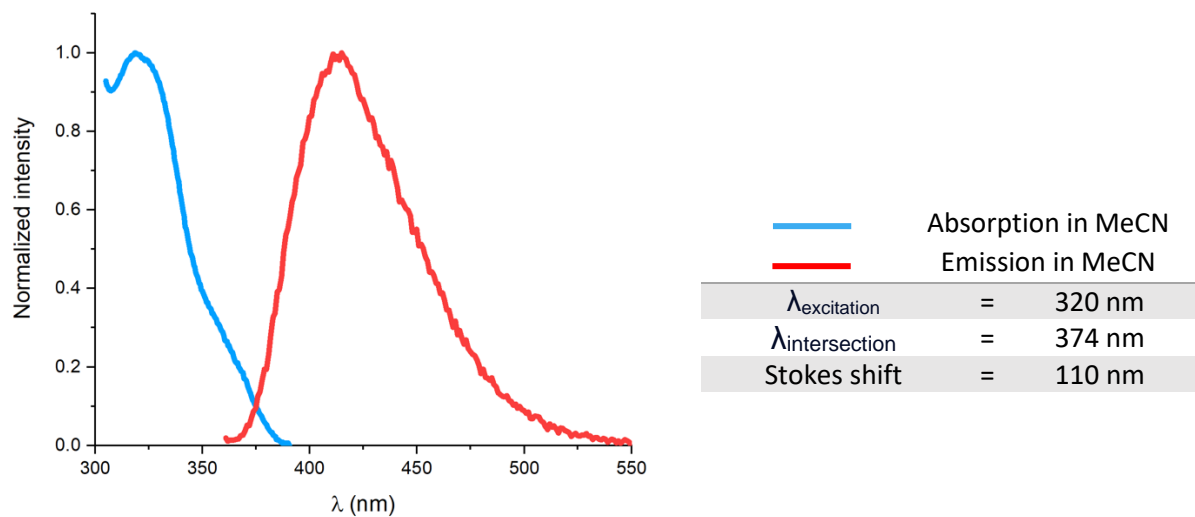


Figure S10: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **5a**.

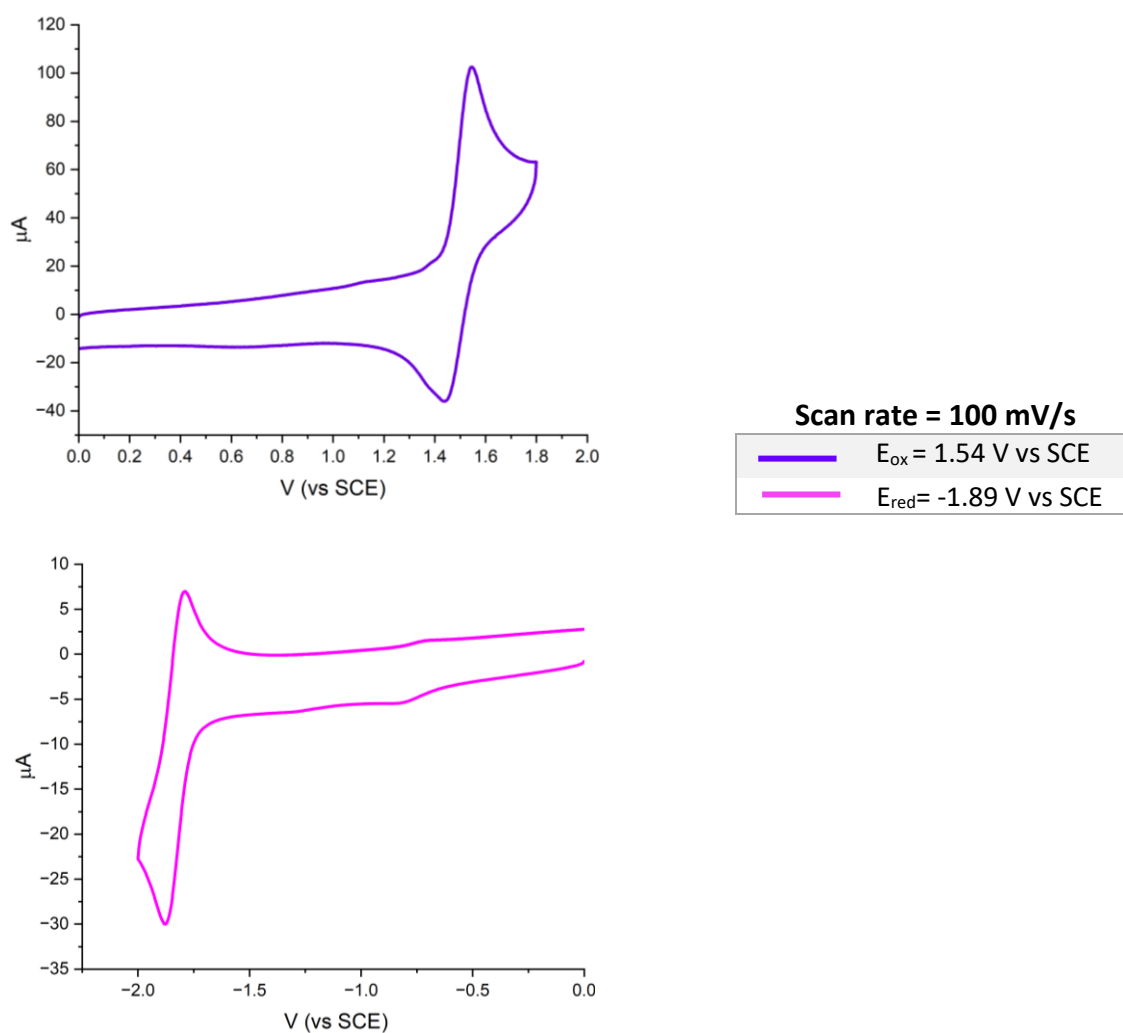


Figure S11: Cyclic voltammograms of **5a** 10^{-3} M . Recorded with GC as the working electrode in MeCN with $0.1 \text{ M } [\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte at 0.1 V/s scan rate.

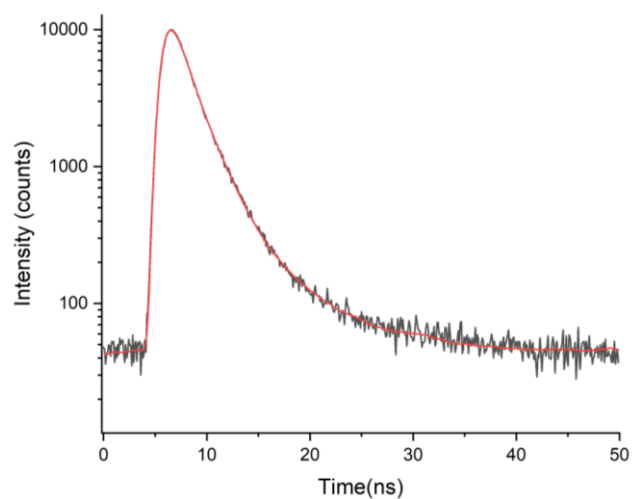


Figure S12: Time-resolved emission decay (excitation at 340 nm) of **5a** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC-SPC ($\tau_1 = 1.6$ ns, $\tau_2 = 5$ ns), from deconvolution and single-exponential fitting, $\chi^2 = 1.23$).

9,9-dimethyl-2-(9H-tribenzo[b,d,f]azepin-9-yl)-9H-thioxanthene 10,10-dioxide (**6a**)

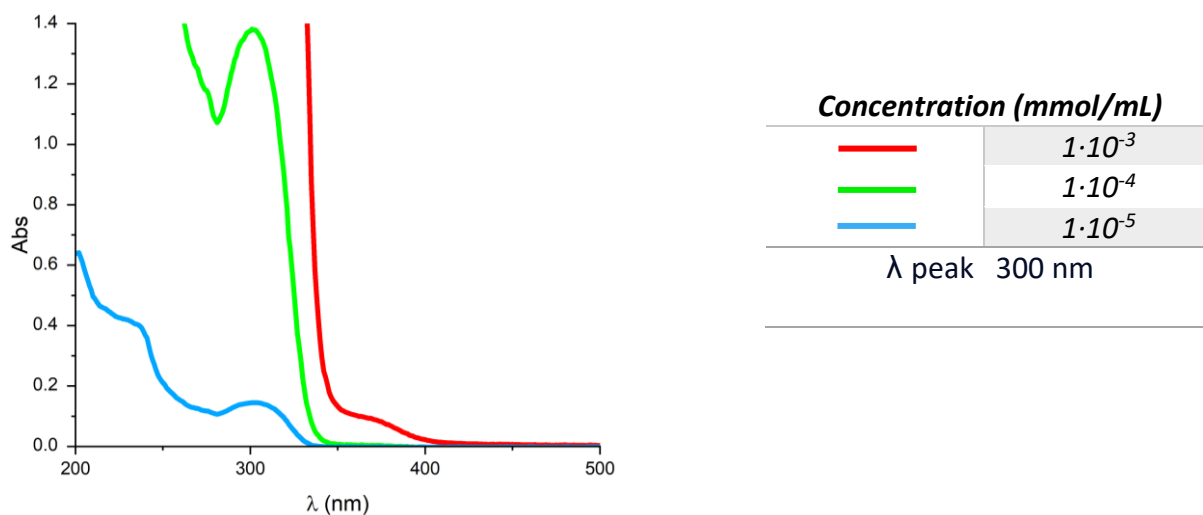
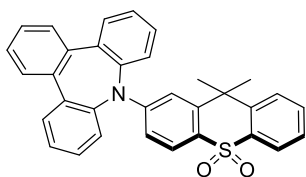


Figure S13: UV-Vis absorption of **6a** at different concentrations. $1 \cdot 10^{-3}$ M (red trace); $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

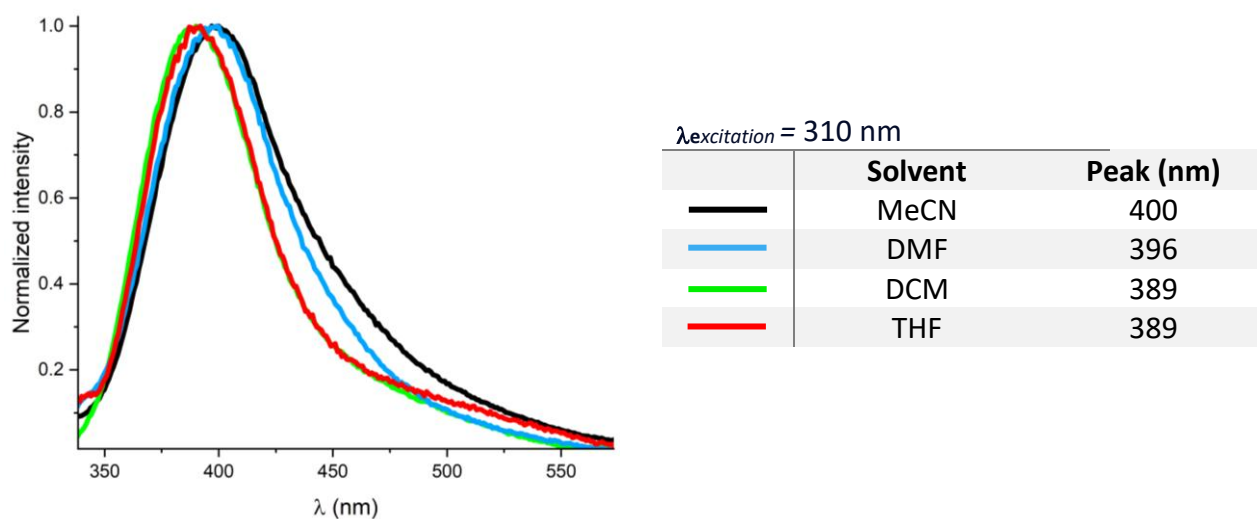


Figure S14: Normalized fluorescence emission of **6a** $1 \cdot 10^{-5}$ M in different solvents. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

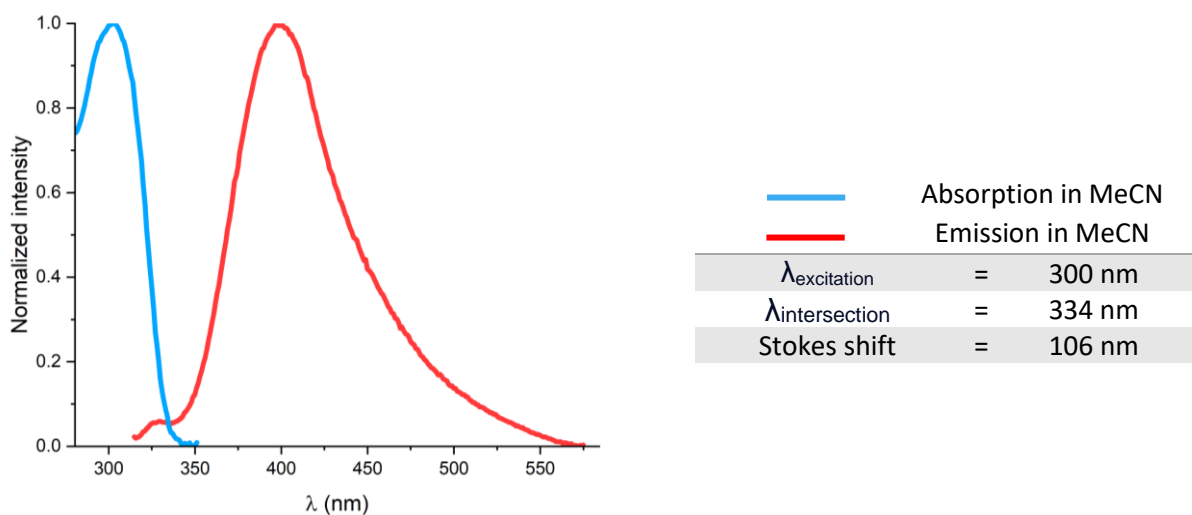


Figure S15: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **6a**.

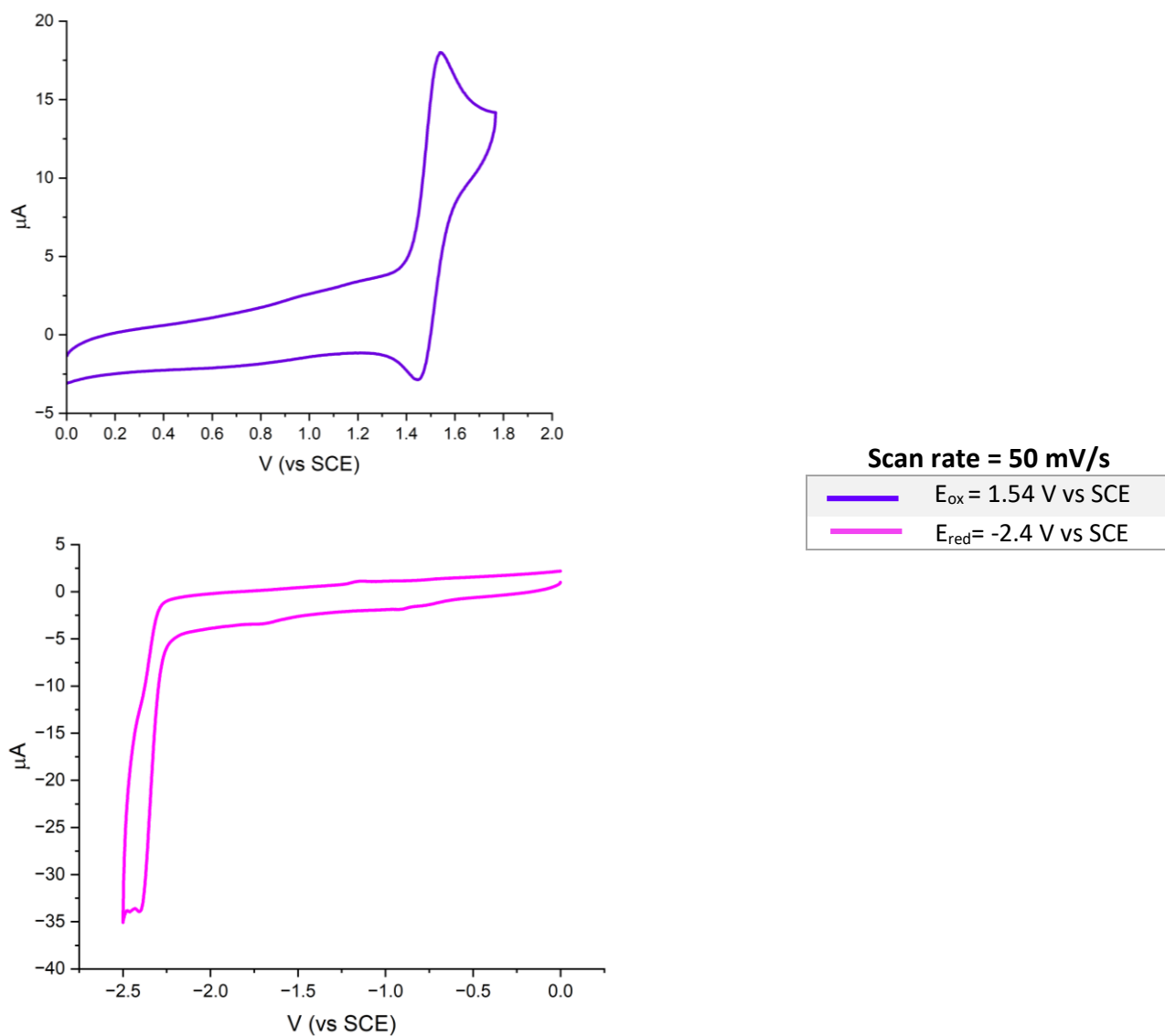


Figure S16: Cyclic voltammograms of **6a** 10^{-3} M . Recorded with GC as the working electrode in MeCN with $0.1 \text{ M [Bu}_4\text{N][PF}_6\text{]}$ as the supporting electrolyte at 0.05 V/s scan rate.

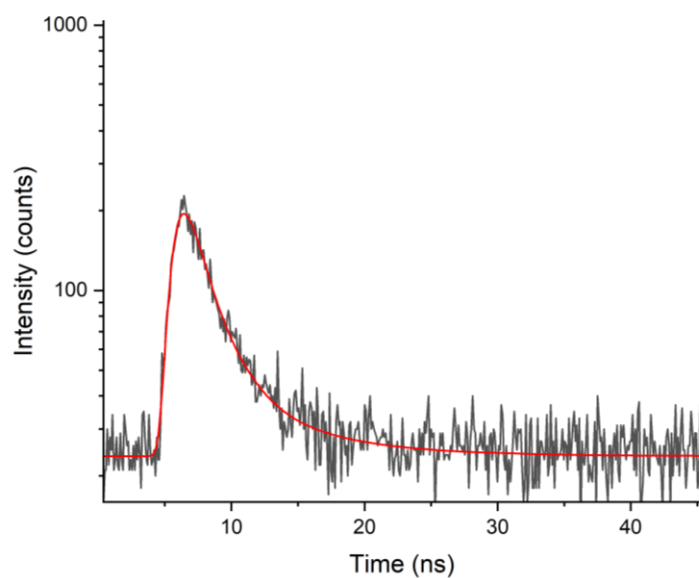


Figure S17: Time-resolved emission decay (excitation at 340 nm) of **6a** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC-SPC ($\tau_1 = 1.68$ ns, $\tau_2 = 6$ ns), from deconvolution and single-exponential fitting, $\chi^2 = 1.12$.

2-(5H-dibenzo[b,f]azepin-5-yl)dibenzo[b,d]thiophene 5,5-dioxide (**5b**)

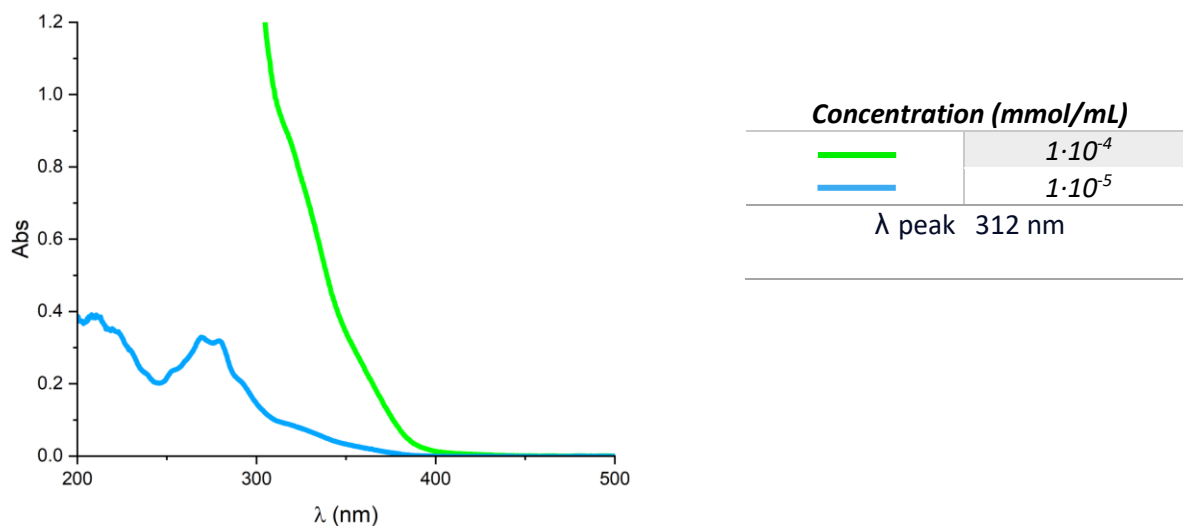
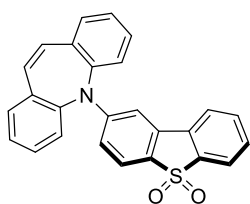


Figure S18: UV-Vis absorption of **5b** at different concentrations $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

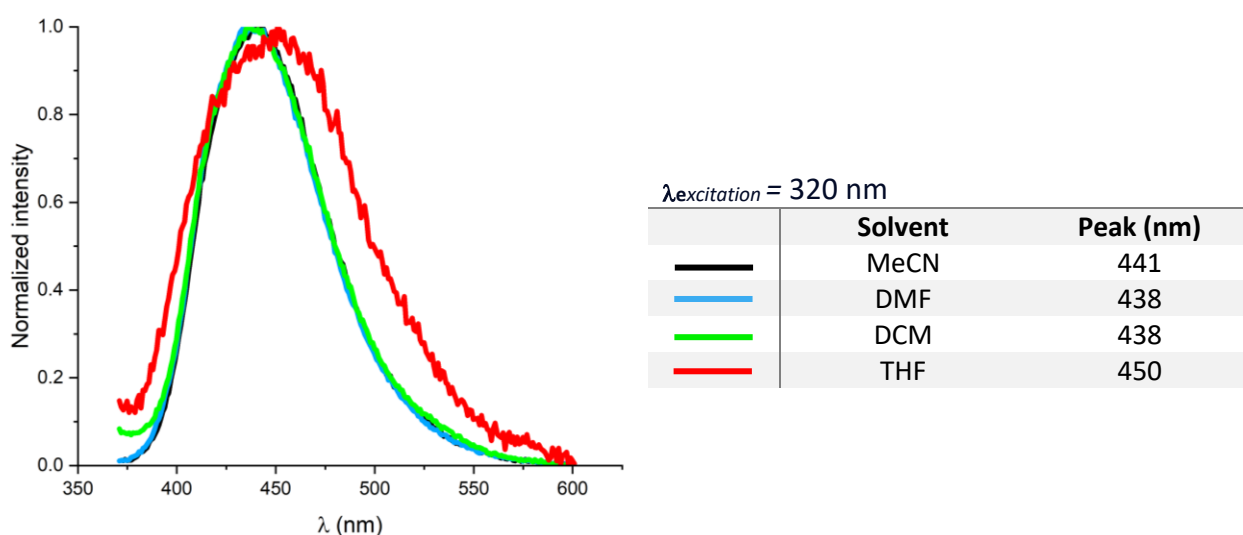


Figure S19: Normalized fluorescence emission of **5b** $1 \cdot 10^{-5}$ M in different solvents. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

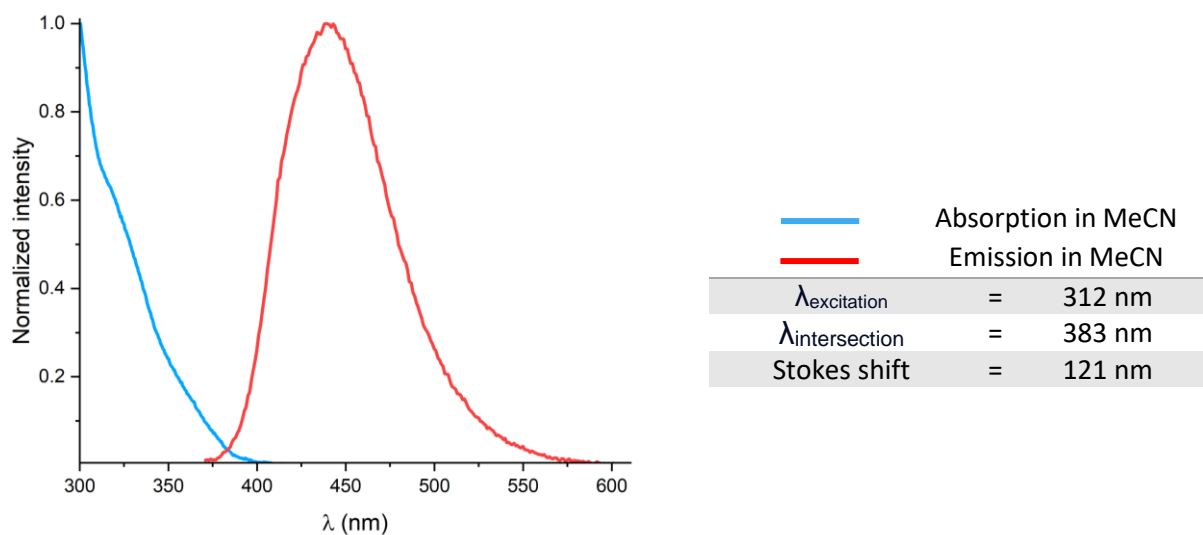


Figure S20: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **5b**.

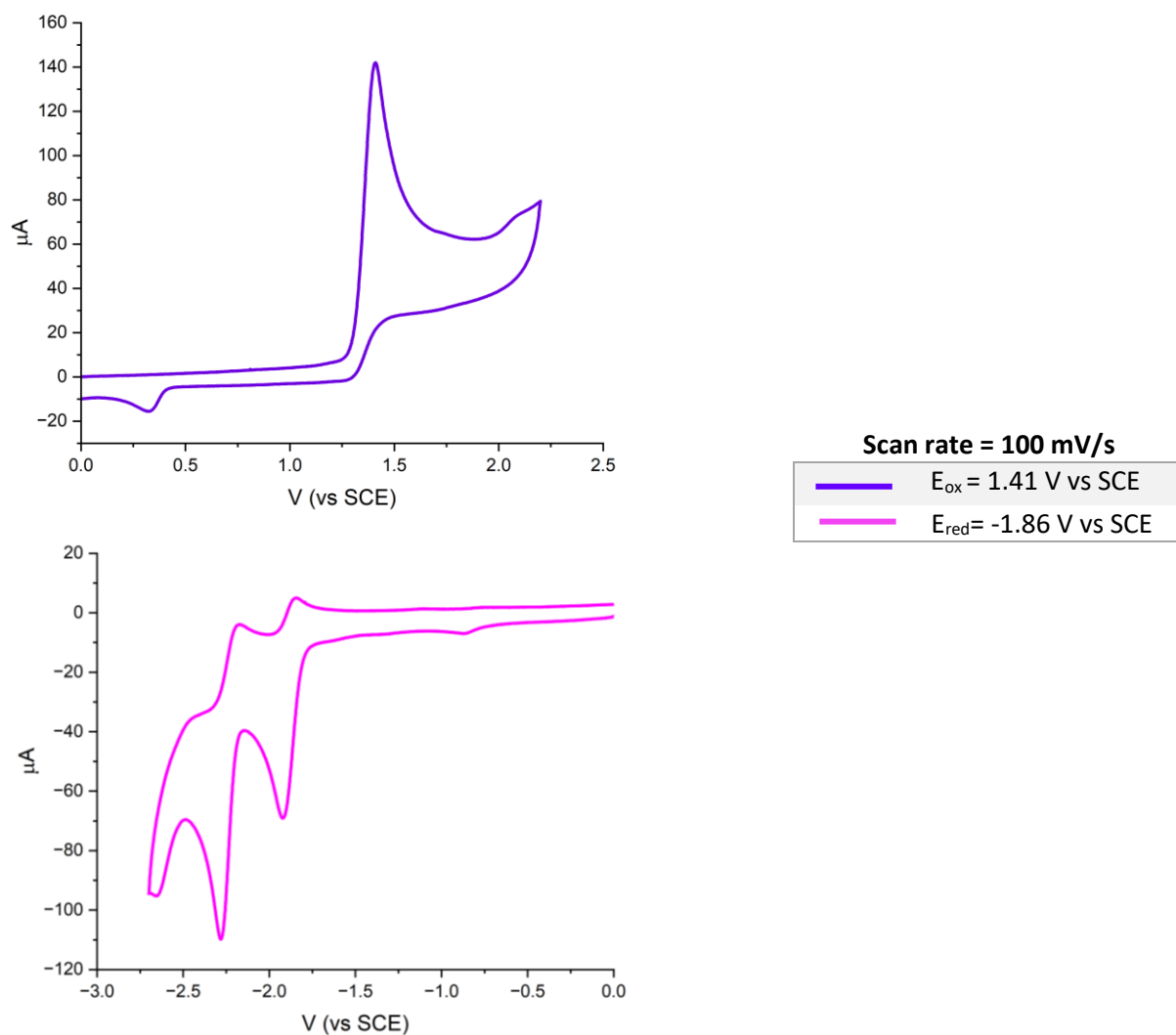


Figure S21: Cyclic voltammograms of **5b** 10^{-3} M . Recorded with GC as the working electrode in MeCN with $0.1 \text{ M [Bu}_4\text{N][PF}_6\text{]}$ as the supporting electrolyte at 0.1 V/s scan rate.

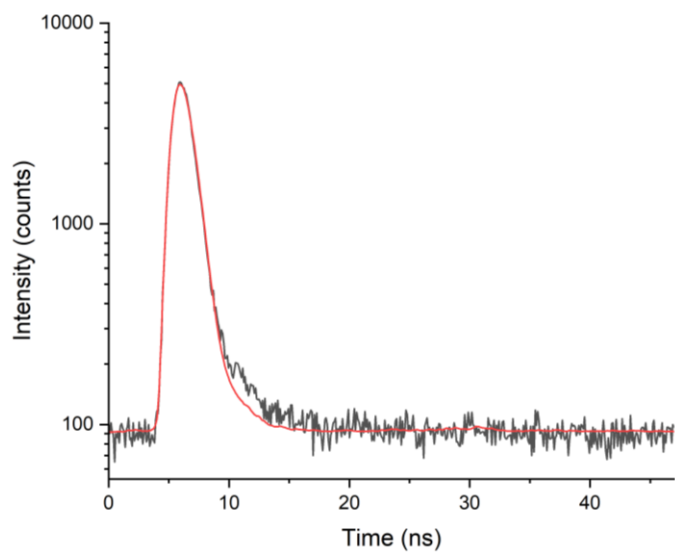


Figure S22: Time-resolved emission decay (excitation at 340 nm) of **5b** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC-SPC ($\tau = 0.7$ ns), from deconvolution and single-exponential fitting, $X^2 = 1.96$).

2-(9*H*-carbazol-9-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**5c**)

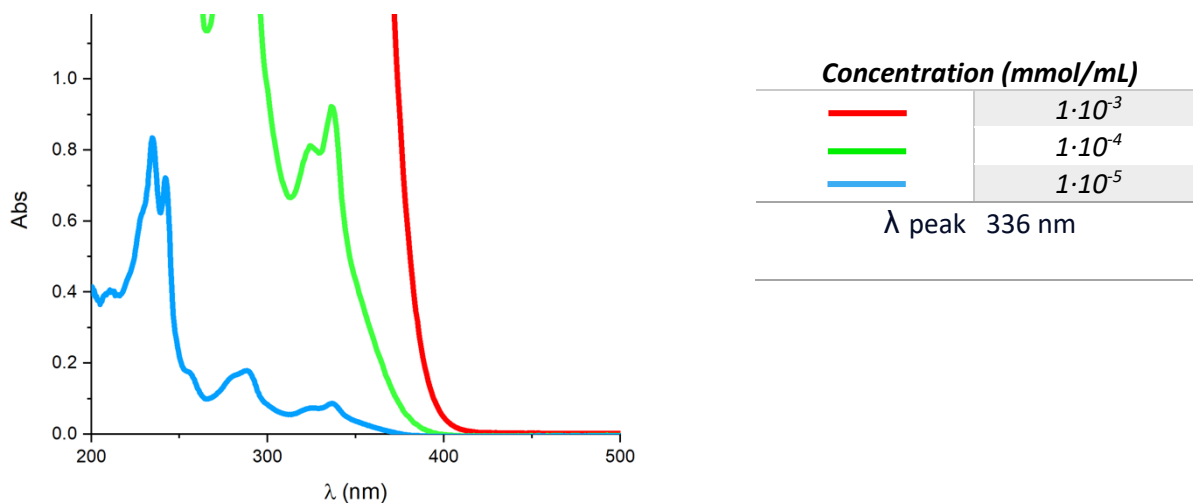
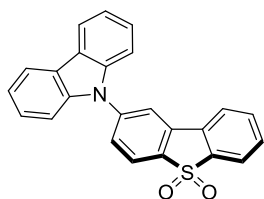


Figure S23: UV-Vis absorption of **5c** at different concentrations. $1 \cdot 10^{-3}$ M (red trace); $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

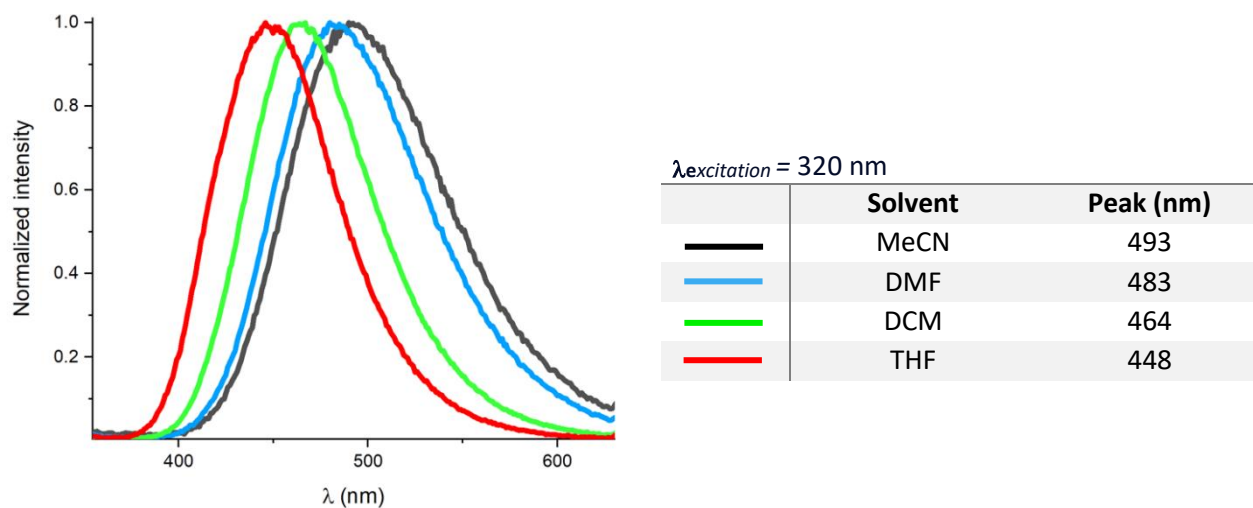


Figure S24: Normalized fluorescence emission of **5c** $1 \cdot 10^{-5}$ M in different solvents. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

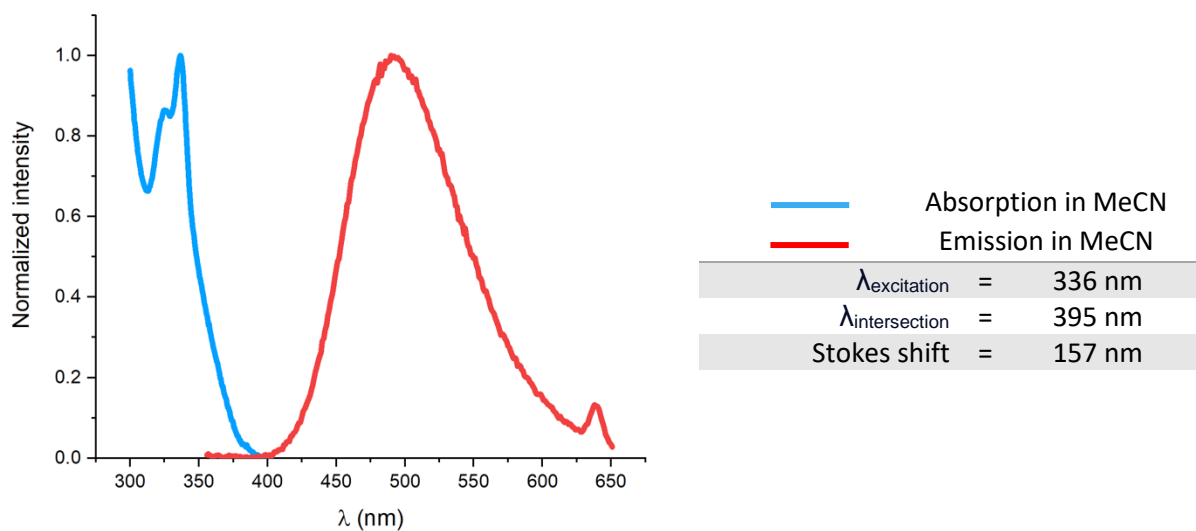


Figure S25: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **5c**.

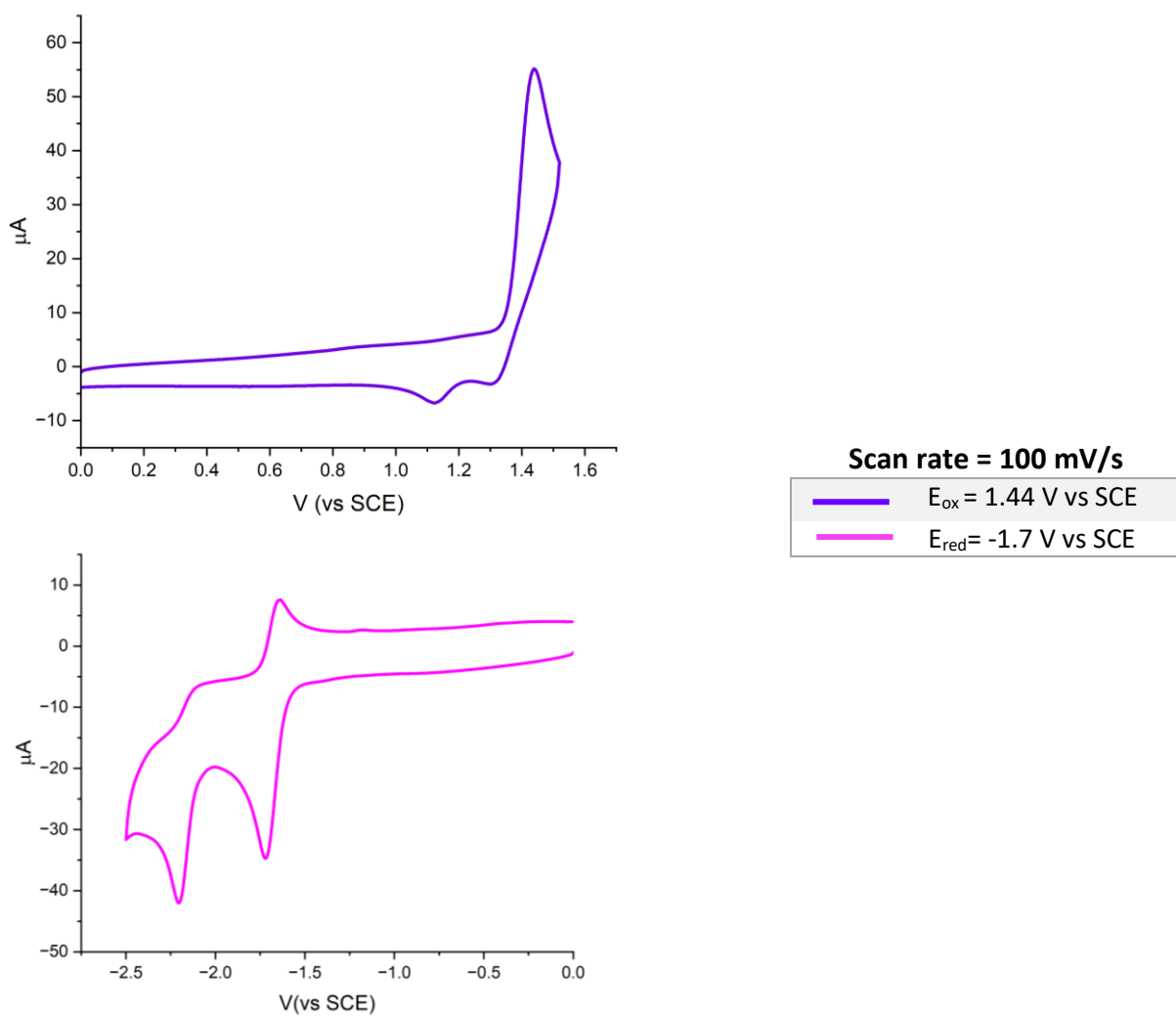


Figure S26: Cyclic voltammograms of **5c** 10^{-3} M . Recorded with GC as the working electrode in MeCN with $0.1 \text{ M } [\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte at 0.1 V/s scan rate.

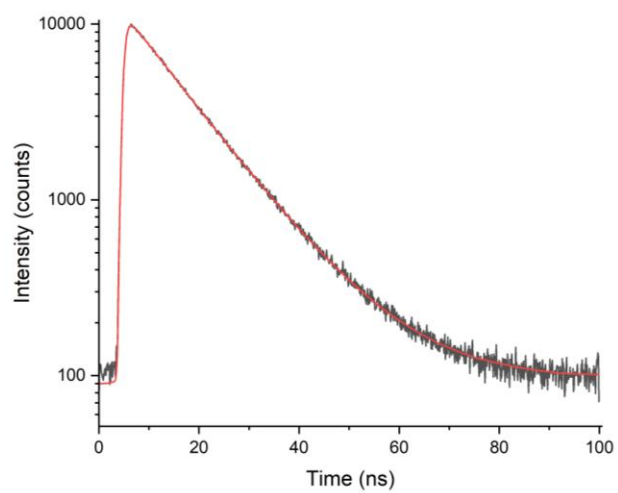


Figure S27: Time-resolved emission decay (excitation at 340 nm) of **5c** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC-SPC ($\tau = 11.6$ ns), from deconvolution and single-exponential fitting, $X^2 = 1.19$.

2-(diphenylamino)dibenzo[*b,d*]thiophene 5,5-dioxide (**5d**)

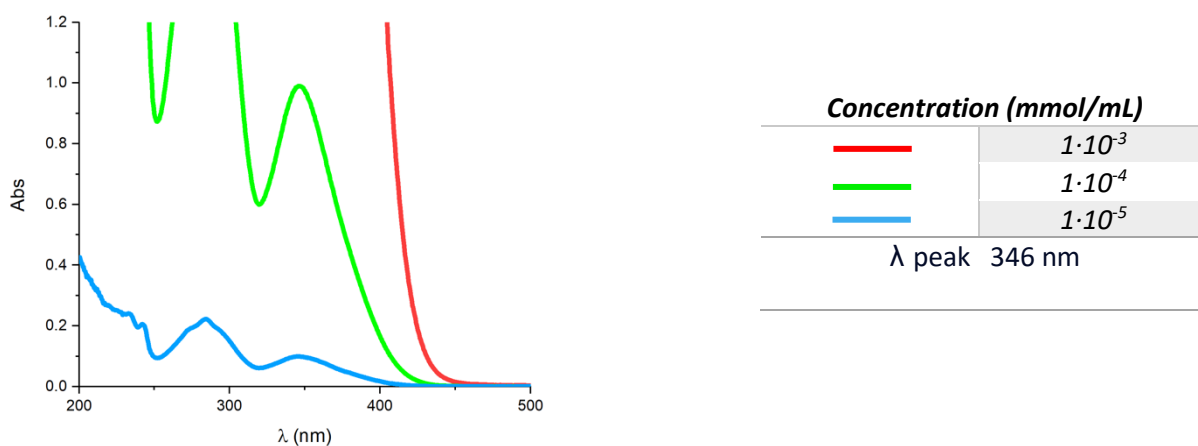
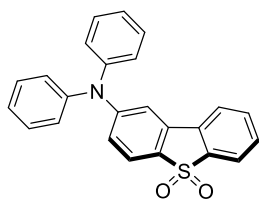


Figure S28: UV-Vis absorption of **5d** at different concentrations. $1 \cdot 10^{-3}$ M (red trace); $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

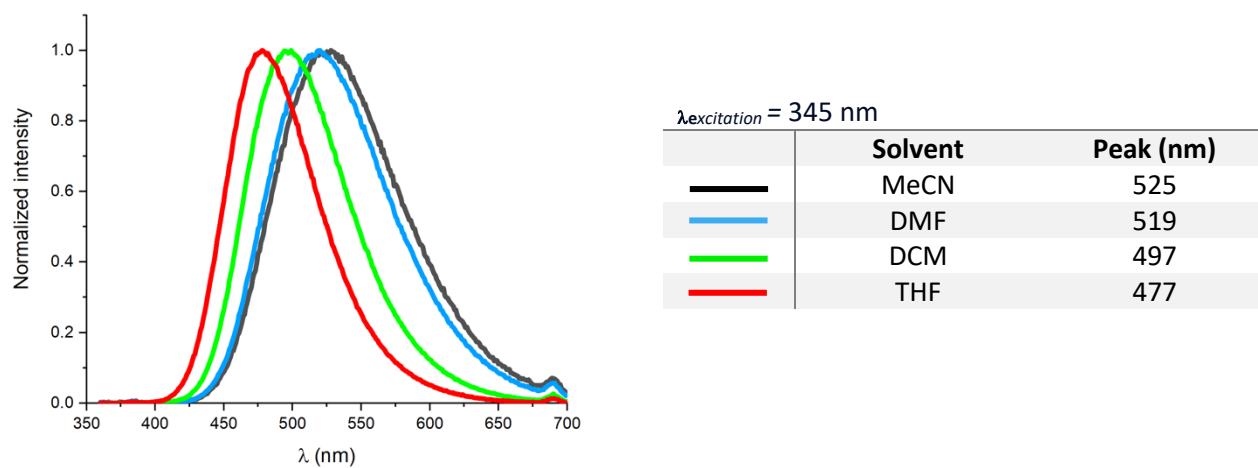


Figure S29: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **5d**.

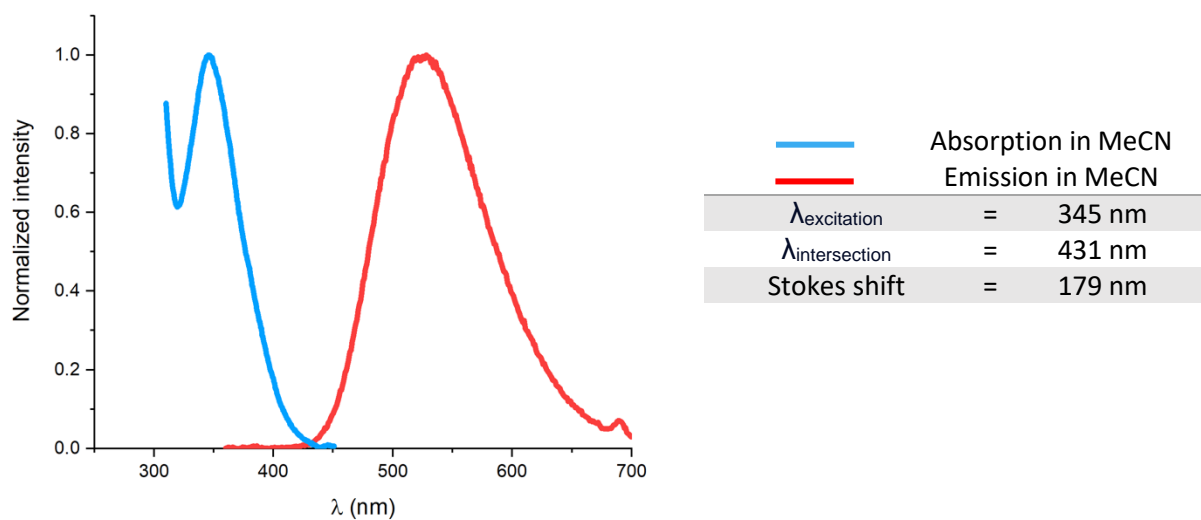


Figure S30: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **5d**.

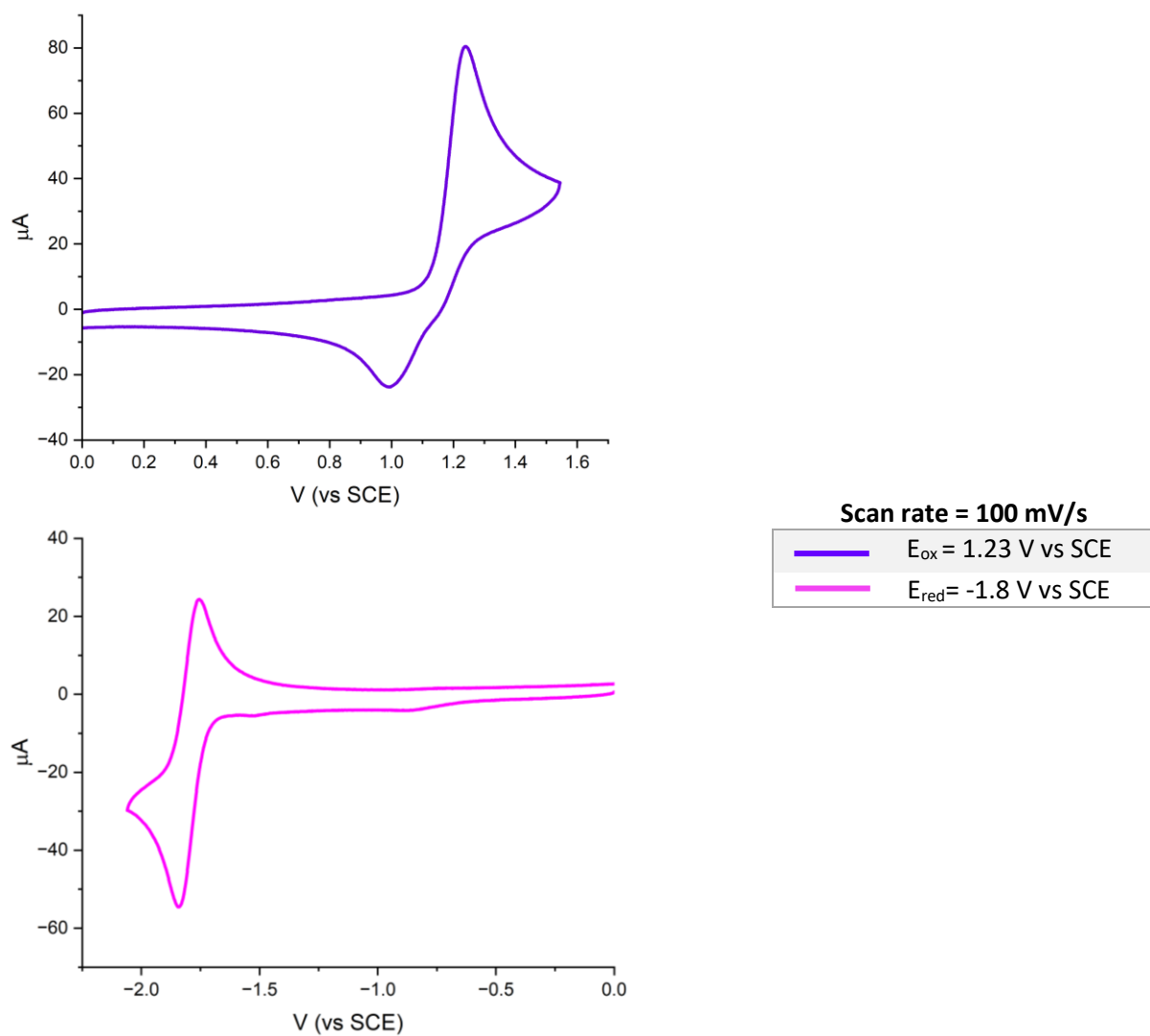


Figure S31. Cyclic voltammograms of **5d** 10^{-3} M . Recorded with GC as the working electrode in MeCN with $0.1 \text{ M } [\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte at 0.1 V/s scan rate.

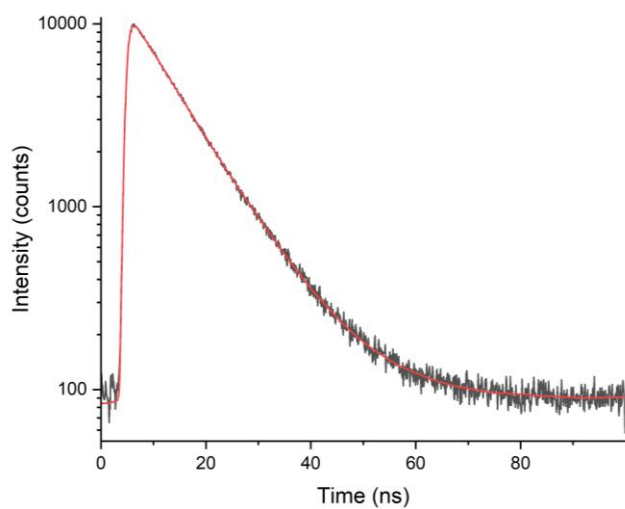


Figure S32: Time-resolved emission decay (excitation at 340 nm) of **5d** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC-SPC ($\tau = 9.3$ ns), from deconvolution and single-exponential fitting, $X^2 = 1.19$).

2-(10*H*-phenoxazin-10-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**5e**)

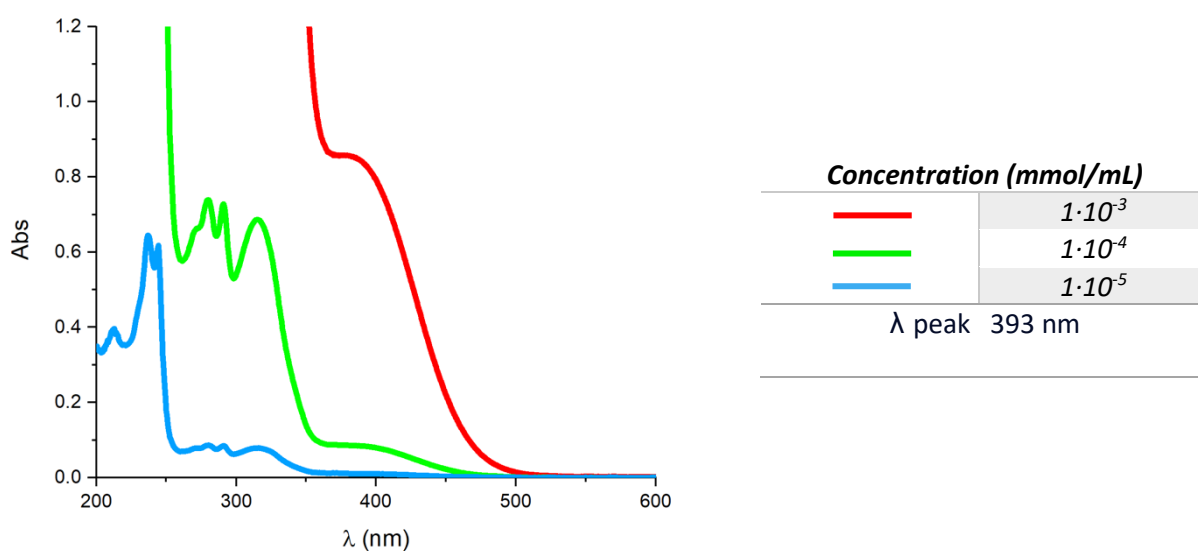
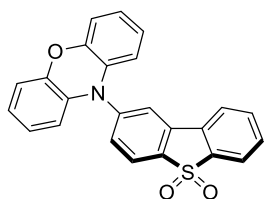


Figure S33: UV-Vis absorption of **5e** at different concentrations. $1 \cdot 10^{-3}$ M (red trace); $1 \cdot 10^{-4}$ M (green trace); $1 \cdot 10^{-5}$ M (blue trace). Recorded in MeCN in quartz cuvettes (1 cm optical path).

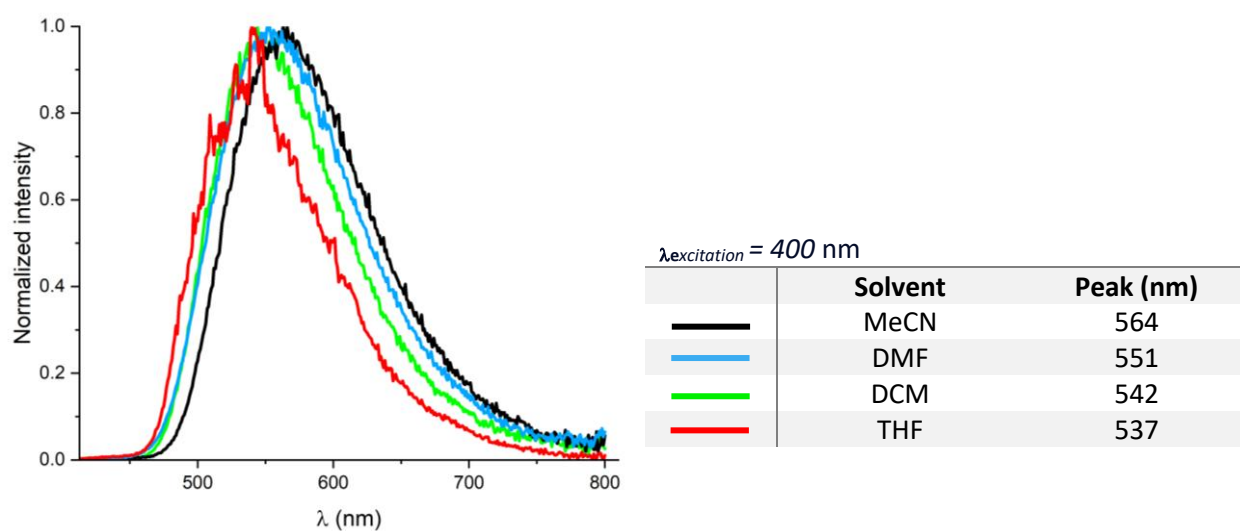


Figure S34: Normalized fluorescence emission of **5e** $1 \cdot 10^{-5}$ M in different solvents at 77K. MeCN (black trace); DMF (blue trace); DCM (green trace); THF (red trace).

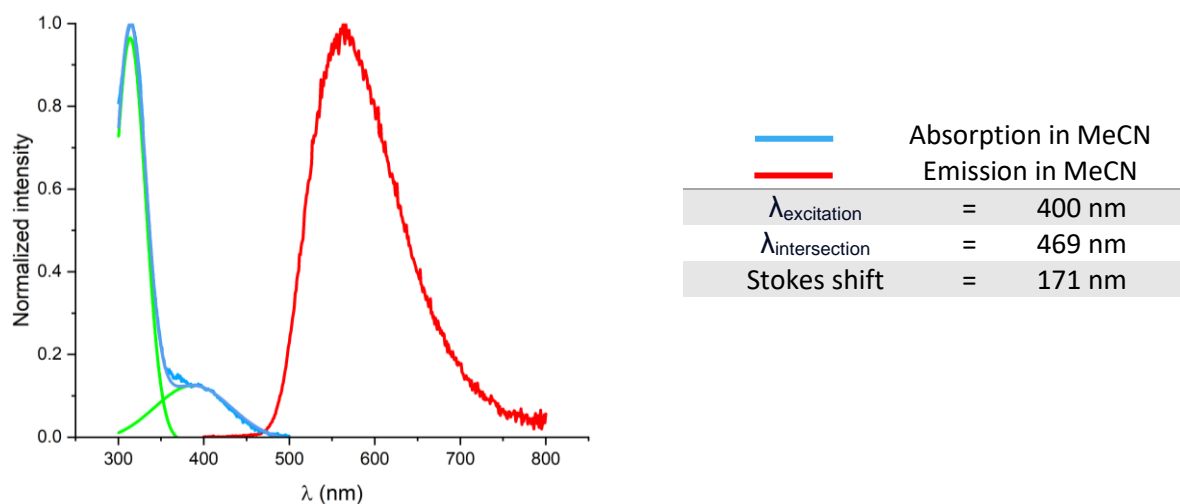


Figure S35: Normalized optical absorption spectrum (blue trace) and emission spectra (red trace) of **5e**. Deconvoluted peaks in green.

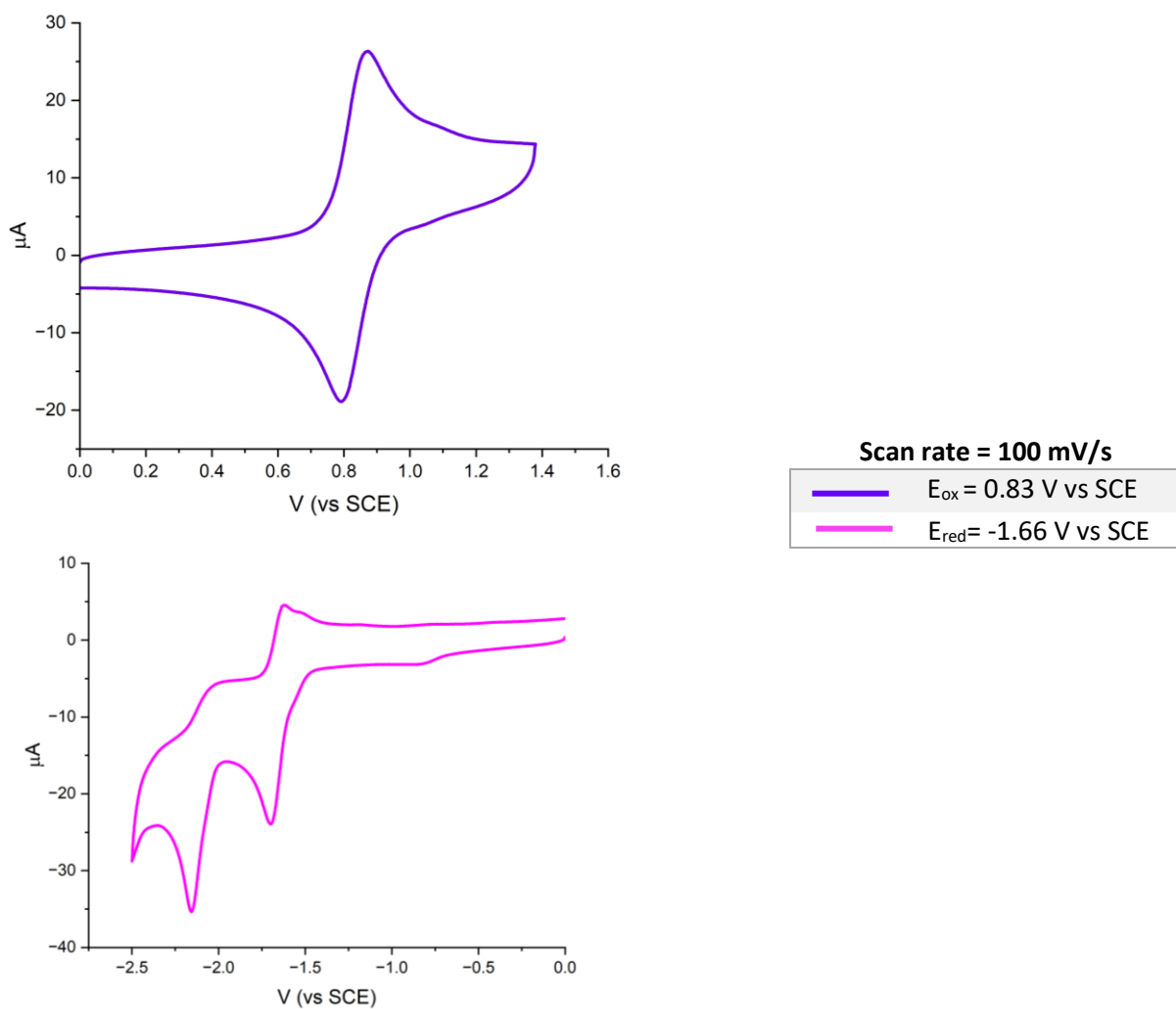


Figure S36: Cyclic voltammograms of **5e** 10^{-3} M . Recorded with GC as the working electrode in MeCN with $0.1 \text{ M } [\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte at 0.1 V/s scan rate

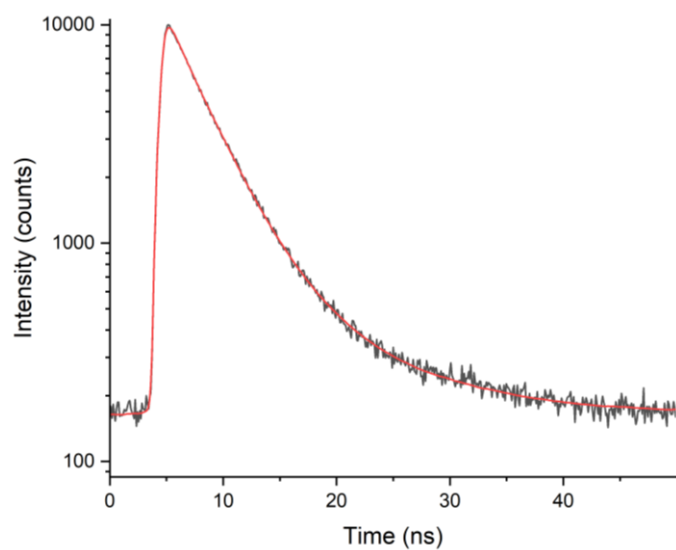
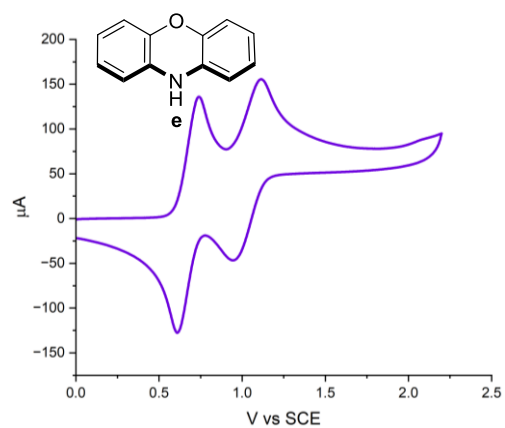
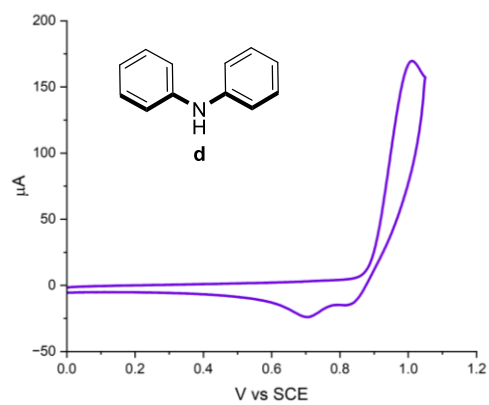
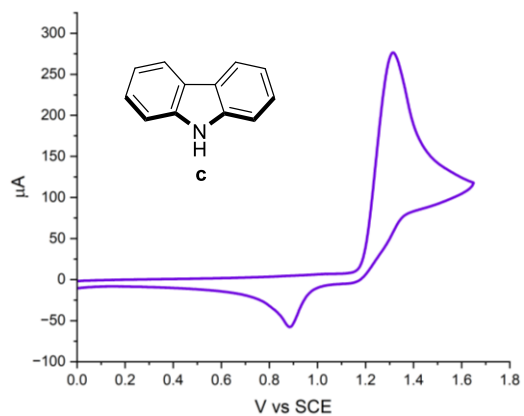
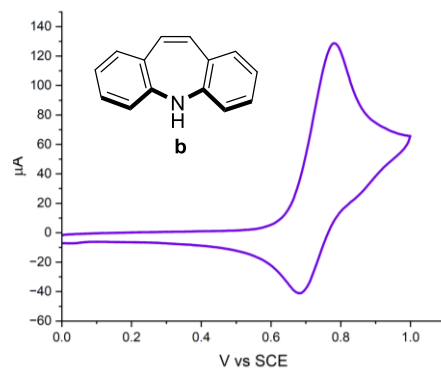
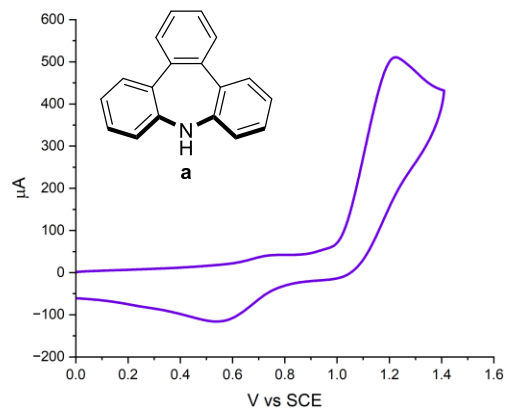


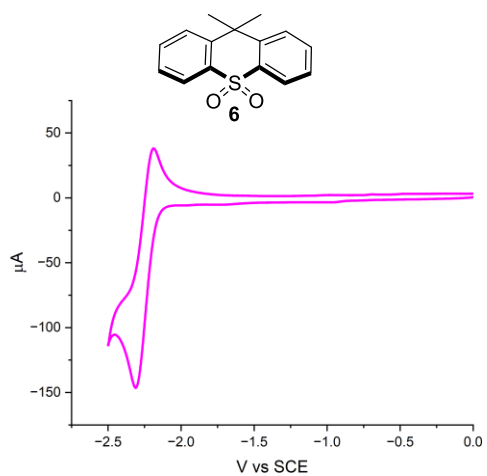
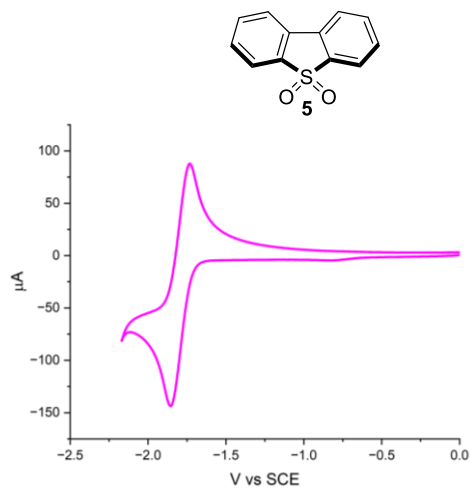
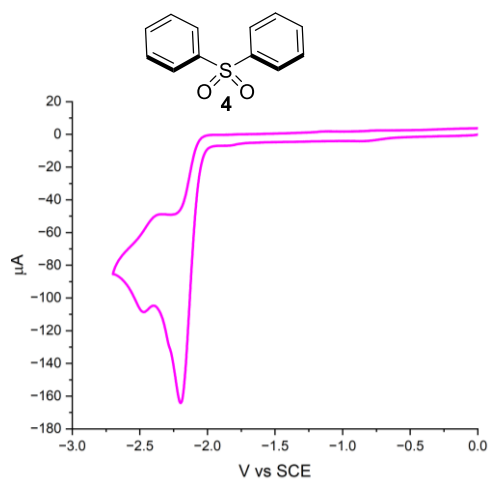
Figure S37. Time-resolved emission decay (excitation at 402.6 nm) of **5e** $1 \cdot 10^{-5}$ M in MeCN solution measured by TC- ($\tau_1 = 3.3$ ns, $\tau_2 = 8.7$ ns), from deconvolution and single-exponential fitting, $\chi^2 = 1.16$).

F. Cyclic voltammograms of donors and acceptors

Donors analysis



Acceptors analysis

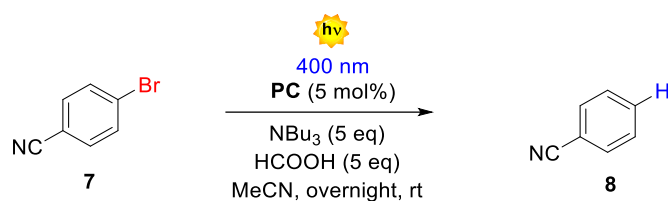


G. Evaluation of the photoredox performances

Oxidative quenching cycle study

General Procedure B

Dehalogenation of *p*-bromobenzonitrile



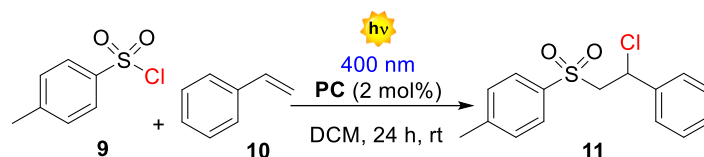
The procedure was followed according to the literature.¹⁴ A 4 mL vial equipped with a septum was charged with a magnetic stirbar, 4-bromobenzonitrile **7** (18.2 mg, 0.1 mmol) and PC (5 mol%) and degassed with Ar. 1 mL of already degassed MeCN was added. Bu_3N (0.12 mL, 5 equiv) and HCOOH (19 μL , 5 equiv) were added via syringe and the reaction mixture was purged with Ar for 1 minute. The vial was irradiated for 12 hours with a 400 nm Kessil lamp set at 100% of its maximum output power.

PC	NMR Yield (%)
4a	N. R.
5a	63%
6a	N.R.
5b	58
5c	56
5d	44
5e	Traces

Table S3: Results of the screening of different PCs in the reductive debromination of 4-bromobenzonitrile **7** according to General procedure B.

General Procedure C

ATRA reaction of toluenesulfonyl chloride and styrene



The procedure was followed according to the literature.¹⁵ To an oven-dried vial was added *p*-toluenesulfonyl chloride (48 mg, 0.25 mmol, 1 equiv.) styrene (0.017 mL, 0.25 mmol, 1 equiv.) and photocatalyst (2 mol%, 0.005 mmol). The vial was purged with a argon for 5 min and dry DCM (1.0 mL) was added before further argon purging for 10 min. The solution was stirred at room temperature while being irradiated a 400 nm Kessil lamp set at 100% of its maximum output power for 24 hours. After removal of solvent, the crude product was purified by flash column chromatography to afford the final product . ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.28-7.21 (7H), 5.32 (t, *J* = 6.9 Hz, 1H), 3.93 (dd, *J* = 14.7, 6.9 Hz, 1H), 3.82 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.40 (s, 3H). The ¹H NMR spectrum is consistent with that in the literature.¹⁵

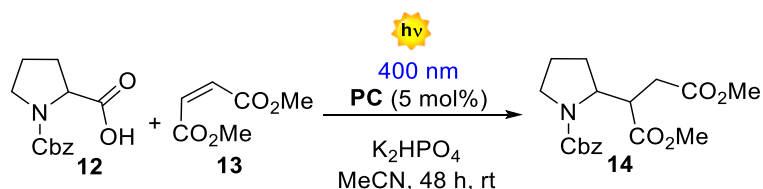
PC	Yield (%)
5a	13%
5b	8%
5c	27 (20)
5d	12
5e	21

Table S4: Results of the screening of different PCs in the reductive ATRA reaction to obtain **11** according to General procedure C. Isolated yield in parenthesis.

Reductive quenching cycle study

General Procedure D

Giese addition



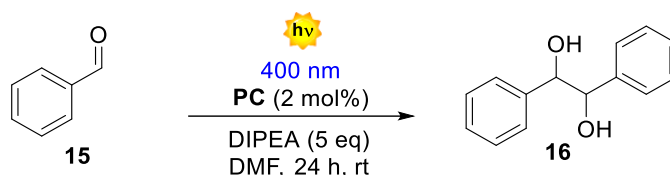
The procedure was followed according to the literature.¹⁶ To an oven dried vial a magnetic stir bar was charged with the selected photocatalyst (0.005 mmol, 5 mol% cat. loading), Cbz-Pro-OH **12** (0.2 mmol, 1.0 equiv), methyl maleate **13** (0.2 mmol, 1.0 equiv), K_2HPO_4 (0.24 mmol, 1.2 equiv), and 0.5 mL of DMF. The reaction mixture was degassed using argon, then irradiated a 400 nm Kessil lamp set at 100% of its maximum output power for 48 h. Then, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution and extracted with Et_2O (3×5 mL). The combined organic extracts were washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel afforded the desired product. 1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.28 (m, 5H), 5.23 – 5.08 (m, 2H), 4.31 (dt, $J = 8.1, 4.9$ Hz, 1H), 4.20 – 4.09 (m, 1H), 3.73 – 3.44 (m, 2H), 3.46 – 3.21 (m, 1H), 2.78 (ddd, $J = 29.0, 16.6, 10.1$ Hz, 1H), 2.62 – 2.30 (m, 1H), 2.07 – 1.72 (m, 4H). The 1H NMR spectrum is consistent with that in the literature.¹⁷

PC	Yield (%)
5a	76 (65)
5b	59
5c	65
5d	43
5e	5

Table S5: Results of the screening of different PCs in the Giese reaction to obtain **14** according to General procedure D. Isolated yield in parenthesis.

General Procedure E

Pinacol coupling



The procedure was followed according to the literature.¹⁵ To an oven-dried vial was added benzaldehyde (0.020 mL, 0.2 mmol, 1 equiv.), DIPEA (0.174 mL, 1 mmol, 5 equiv.) and photocatalyst (2 mol%, 0.004 mmol). The vial was purged with argon for 5 min and dry DMF (2.0 mL) was added before further argon purging for 10 min. The reaction mixture was stirred at room temperature while being irradiated 400 nm Kessil lamp set at 100% of its maximum output power for 24 h. After removal of solvent, the crude product was purified by flash column to afford the product **18**. **¹H NMR (400 MHz, CDCl₃)** δ 7.33 (m, 7H), 7.31 – 7.21 (m, 11H), 7.15 (dd, J = 6.6, 3.0 Hz, 4H), 4.86 (s, 2H), 4.74 (s, 2H), 2.87 (s, 2H), 2.24 (s, 2H). The ¹H NMR spectrum is consistent with that in the literature.¹⁵

PC	Yield (%)
5a	69 (60)
5b	41
5c	55
5d	51
5e	51

Table S6: Results of the screening of different PCs in the pinacol coupling to obtain **16** according to General procedure E. Isolated yield in parenthesis.

H. Theoretical studies

DFT calculations

All the calculations were performed with the GAUSSIAN16 suite of programs (Revision C.01). Each geometry was optimized with default convergence thresholds (RMS values of 3×10^{-4} hartree/bohr and 1.2×10^{-3} bohr and maximum values of 4.5×10^{-4} hartree/bohr and 1.8×10^{-3} bohr on forces and displacements, respectively) at B3LYP/Def2TZVP EmpiricalDispersion=GD3 level of theory. Polarization effects were taken into account with the polarizable continuum model (PCM).

Optimized geometries and SCF energies

4a

SCF energy: -1759.848854 Hartree
Neutral singlet, total number of atoms: 55
C 4.97154500 -0.01497700 0.18085200
C 5.36805800 -1.17939800 -0.47160800
C 1.62060300 1.15448300 0.61254300
C 2.24345300 -0.07322100 0.84052500
S 3.84823600 -0.12762200 1.56364400
O 4.02840300 1.06406100 2.37163900
O 4.03206400 -1.43226900 2.17170700
C 5.41406900 1.23609200 -0.23972500
C 6.26958900 1.31829600 -1.33195300
C 6.67156000 0.16111000 -1.99340600
C 6.22307500 -1.08488300 -1.56279200
C 0.37641300 1.20287600 0.01608900
C -0.27919000 0.01774900 -0.37859600
C 0.36251600 -1.21447100 -0.13536400
C 1.60704300 -1.25536500 0.46110100
N -1.51712500 0.06210300 -0.98115900
C -2.27400200 1.26937900 -1.10208700
C -3.26760600 1.54257000 -0.15192000
C -3.48539800 0.65291600 1.01314900
C -3.49339400 -0.75923100 0.92253000
C -3.28255300 -1.49499300 -0.34645700
C -2.28517900 -1.11291500 -1.25417700
C -2.03984400 2.12797200 -2.17118800
C -2.79391800 3.28485600 -2.31151900
C -3.79510900 3.56821200 -1.38572900
C -4.02885900 2.70708400 -0.32281700
C -3.71545000 1.24693400 2.26210400
C -3.94599000 0.49039100 3.39999400
C -3.95518500 -0.89782300 3.31069900
C -3.73271800 -1.50535500 2.08525200
C -4.05497200 -2.62060100 -0.66430400
C -3.82871300 -3.34178400 -1.82813000
C -2.82370000 -2.95287900 -2.71039700
C -2.05847000 -1.83083000 -2.42397000
H 5.01940300 -2.14307600 -0.12605400
H 2.10574100 2.07341800 0.91336600
H 5.10043100 2.12857500 0.28430700
H 6.62336400 2.28602400 -1.66412800

H 7.33813400 0.22977800 -2.84398200
H 6.54063400 -1.98442000 -2.07464200
H -0.09798800 2.16062700 -0.14084400
H -0.12321300 -2.13944000 -0.40984900
H 2.08167500 -2.20993500 0.64431900
H -1.26116600 1.87982300 -2.88104400
H -2.60943700 3.95483900 -3.14164600
H -4.40040000 4.45928300 -1.49612700
H -4.81976600 2.93149400 0.38120000
H -3.69264700 2.32616500 2.34002800
H -4.10577700 0.98134100 4.35184600
H -4.12271800 -1.50434100 4.19196000
H -3.72373600 -2.58596400 2.02462000
H -4.84927500 -2.92444500 0.00514400
H -4.44289700 -4.20524500 -2.05133100
H -2.64497300 -3.51314300 -3.61937700
H -1.27704600 -1.50162500 -3.09692200

5a

SCF energy: -1758.642303 Hartree

Neutral singlet, total number of atoms: 53

C 4.42932700 0.07155200 0.08961500
C 3.28391000 0.81821400 -0.19679400
C 2.08325500 -0.01986200 -0.37607200
C 2.34553500 -1.38444700 -0.21757900
S 4.04774600 -1.66748600 0.14366900
O 4.71619400 -2.37783400 -0.93255000
O 4.23349400 -2.19750100 1.48308000
C 5.66992800 0.64328800 0.29709400
C 5.76481900 2.03144100 0.21424200
C 4.63559000 2.79819600 -0.06940300
C 3.39348400 2.20232300 -0.27635200
C 0.79952600 0.40464100 -0.66397000
C -0.23802300 -0.54113200 -0.79672900
C 0.05521400 -1.91181900 -0.62457900
C 1.34286800 -2.33229800 -0.33691000
N -1.52172100 -0.12981200 -1.09213600
C -1.89956300 1.25012800 -1.08539800
C -2.43186600 1.80094100 0.08871000
C -2.53046800 1.00671300 1.33600500
C -2.97151100 -0.33765600 1.36900900
C -3.38124500 -1.09064000 0.15999500
C -2.64284000 -1.01648100 -1.02938700
C -1.76288600 2.00841900 -2.24312100
C -2.15476100 3.34021400 -2.25190100
C -2.69894600 3.90300500 -1.10012200
C -2.83667400 3.14222600 0.05250600
C -2.18462300 1.62979200 2.54355200
C -2.25984800 0.96468600 3.75693500
C -2.69324300 -0.35676000 3.78935400
C -3.04384300 -0.99022800 2.60777100
C -4.50351100 -1.92996000 0.17784500
C -4.86157300 -2.67363800 -0.93800700
C -4.10696300 -2.59495800 -2.10583300
C -3.00070500 -1.75738600 -2.15048900

H 6.53878600 0.03616600 0.51689600
H 6.72065600 2.51410300 0.37152900
H 4.72453900 3.87549400 -0.13016900
H 2.52480700 2.80932300 -0.49552800
H 0.59193600 1.45800200 -0.78184500
H -0.73332300 -2.64443100 -0.71376800
H 1.55111800 -3.38668000 -0.20605500
H -1.34376500 1.54374900 -3.12645600
H -2.04620100 3.93136900 -3.15232600
H -3.02403100 4.93589200 -1.10188900
H -3.27531000 3.58766600 0.93603100
H -1.83022100 2.65220500 2.52261400
H -1.97089400 1.47126800 4.66932500
H -2.74662200 -0.89522900 4.72728900
H -3.36414800 -2.02359800 2.63655100
H -5.10746600 -1.98872200 1.07413800
H -5.73617200 -3.31095600 -0.89884100
H -4.38400000 -3.17403000 -2.97760300
H -2.40127000 -1.67155500 -3.04778100

6a

SCF energy: -1876.631801 Hartree

Neutral singlet, total number of atoms: 62

C 5.98717600 0.52600400 1.80866200
C 5.53384900 1.80422300 1.50824100
C 4.46221900 1.99249700 0.64232500
C 3.80497400 0.91842200 0.03492100
C 4.28846200 -0.35757400 0.35990300
C 5.35256900 -0.56346600 1.23330000
C 2.65621000 1.13440000 -0.96764300
C 1.57800400 0.04347700 -0.82493900
C 1.90170000 -1.29839800 -0.56246900
S 3.56717300 -1.80571200 -0.36100500
C 0.23220800 0.34476200 -0.98515000
C -0.77797900 -0.62978700 -0.89973600
C -0.41508500 -1.96036000 -0.63136800
C 0.91526700 -2.27822300 -0.46022900
N -2.10406900 -0.27451000 -1.07043700
C -2.51335700 1.09631500 -1.12327600
C -2.82459100 1.75928900 0.07230800
C -2.65945400 1.09312200 1.38561100
C -3.05123500 -0.24400000 1.63392000
C -3.66493300 -1.11772000 0.60603300
C -3.17041000 -1.15724900 -0.70566700
C -2.61821300 1.73643300 -2.35311900
C -3.03769400 3.05855500 -2.41531000
C -3.36459300 3.73077000 -1.24038200
C -3.26036500 3.08827100 -0.01441900
C -2.09844100 1.83462300 2.43499100
C -1.91816400 1.29303800 3.69771200
C -2.30513300 -0.02058400 3.94240000
C -2.86447300 -0.77027700 2.91991800
C -4.73830500 -1.96095700 0.92278500
C -5.28350500 -2.81591400 -0.02517200
C -4.76987600 -2.84842500 -1.31906900

C -3.71571200 -2.01058800 -1.65809500
O 4.18977200 -2.04990600 -1.65441400
O 3.62775900 -2.89838400 0.59399400
C 2.04839700 2.53760300 -0.81275700
C 3.24311600 1.05359100 -2.40591900
H 6.81611500 0.37702100 2.48828700
H 6.00937800 2.66797900 1.95601300
H 4.14021600 3.00365700 0.44825800
H 5.66954300 -1.57188600 1.46404400
H -0.06914500 1.36177500 -1.16679000
H -1.16841900 -2.72942100 -0.54251700
H 1.19617200 -3.29791900 -0.23176500
H -2.36274700 1.18832700 -3.25103100
H -3.11726400 3.55787800 -3.37258500
H -3.70833900 4.75687200 -1.27960600
H -3.53088900 3.61790200 0.88992200
H -1.77925100 2.85118800 2.24514900
H -1.46725600 1.88850600 4.48170000
H -2.16064800 -0.46334400 4.91998100
H -3.14598300 -1.79771600 3.11094900
H -5.15562300 -1.93541800 1.92117100
H -6.11607300 -3.45361700 0.24467300
H -5.19264700 -3.51508000 -2.05996200
H -3.30158300 -2.01066000 -2.65826800
H 1.60526900 2.68613300 0.17303200
H 2.80690700 3.30089100 -0.97392400
H 1.28392400 2.70756200 -1.56847600
H 3.99922200 1.83012600 -2.53524800
H 3.70061100 0.08787200 -2.60730900
H 2.44617400 1.21942200 -3.13308500

5b

SCF energy: -1604.927533 Hartree

Neutral singlet, total number of atoms: 47

C -0.63238400 -0.46483600 -0.34459400
C -0.35129000 -1.84667700 -0.25558300
C 0.94906900 -2.30286100 -0.11678500
C 1.98059500 -1.38087000 -0.06327500
C 1.73304100 -0.00688500 -0.13809400
C 0.43675600 0.45318800 -0.27596900
S 3.70454100 -1.70856800 0.10925200
C 4.11547700 0.02476700 0.08934400
C 2.96308900 0.80221800 -0.04859100
C 5.38239700 0.56637300 0.19265000
C 5.49772200 1.95494800 0.15604400
C 4.36219100 2.75191100 0.01855800
C 3.09324700 2.18633700 -0.08470800
N -1.93244000 -0.01638100 -0.49763400
C -2.24722700 1.37552300 -0.41330100
C -2.65766500 1.91435700 0.81820800
C -2.91735600 1.08879300 1.99226400
C -3.36134000 -0.18355400 2.01622600
C -3.68659200 -1.02975800 0.87329900
C -3.04418400 -0.90608600 -0.37071800
C -4.70450400 -1.99011900 0.99201400

C -5.09367500 -2.76114000 -0.09185100
C -4.47142900 -2.59455000 -1.32839200
C -3.44707800 -1.66725400 -1.46337900
C -2.09664500 2.18534200 -1.53456500
C -2.31451400 3.55331500 -1.44181900
C -2.68306600 4.11258900 -0.21890200
C -2.85032500 3.30343700 0.89373800
O 4.01408300 -2.30043200 1.39893500
O 4.24453100 -2.38166800 -1.05905600
H -1.15723300 -2.56387500 -0.29248700
H 1.14404400 -3.36567500 -0.04917200
H 0.24759800 1.51476500 -0.32602100
H 6.25603900 -0.06384000 0.29864600
H 6.47456100 2.41408800 0.23500700
H 4.46741000 3.82909400 -0.00872200
H 2.22029100 2.81686900 -0.19198000
H -2.83962200 1.60403400 2.94394900
H -3.60972900 -0.60284900 2.98565600
H -5.19797800 -2.11359200 1.94869800
H -5.88504900 -3.49122900 0.02338500
H -4.77381900 -3.19358400 -2.17795800
H -2.93065800 -1.54221300 -2.40658000
H -1.78044400 1.73427600 -2.46654400
H -2.18476100 4.18184600 -2.31367100
H -2.84307600 5.18040800 -0.13694700
H -3.14793300 3.73896800 1.84018500

5c

SCF energy: -1527.503961 Hartree

Neutral singlet, total number of atoms: 43

C 5.26186600 1.94775200 -1.41640500
C 4.05517600 2.54970100 -1.77016700
C 2.83522100 2.00272200 -1.37960200
C 2.82802300 0.83583600 -0.62368000
C 4.04972700 0.25158400 -0.28078300
C 5.26999000 0.77842400 -0.65828100
C 1.66739000 0.09107000 -0.10443800
C 2.02567000 -1.04617000 0.62286600
S 3.79296500 -1.21948800 0.68627200
C 0.32219500 0.38611300 -0.27025000
C -0.63394500 -0.45070700 0.30932100
C -0.25183900 -1.57945900 1.04035800
C 1.09384400 -1.89070800 1.19509600
O 4.22764200 -2.40118100 -0.03270300
O 4.28688600 -1.04717900 2.03855800
N -2.00614600 -0.14958700 0.15412500
C -2.61137200 1.07158600 0.45590600
C -3.99187300 0.98240600 0.16336000
C -4.22847000 -0.34949100 -0.34156200
C -2.98362600 -1.02012200 -0.33118400
C -2.05578900 2.22912900 0.99684000
C -2.90312600 3.30610600 1.22473400
C -4.27173000 3.23777100 0.92720300
C -4.82266300 2.07801500 0.40052300
C -5.36697100 -1.00861000 -0.80647600

C -5.24988200 -2.31604100 -1.25676600
C -4.00581600 -2.96296500 -1.25304800
C -2.85840800 -2.32805700 -0.79468200
H 6.19869900 2.38889400 -1.73075700
H 4.06530300 3.45792800 -2.35919300
H 1.90506100 2.47914700 -1.66057000
H 6.19969300 0.30095100 -0.37672000
H 0.01043800 1.24664800 -0.84558500
H -1.00901700 -2.20422600 1.49288300
H 1.39502800 -2.76279500 1.76065700
H -1.00343600 2.29213100 1.23667000
H -2.49410500 4.21733400 1.64338900
H -4.90242400 4.09729400 1.11625400
H -5.88129300 2.01815000 0.17945300
H -6.32424200 -0.50205600 -0.81778900
H -6.12396900 -2.84227700 -1.61921200
H -3.93387800 -3.98067400 -1.61640300
H -1.90405900 -2.83594600 -0.80245000

5d

SCF energy: -1528.689691 Hartree
Neutral singlet, total number of atoms: 45
C -5.29661900 1.92331000 -0.87118200
C -4.13601200 2.66311400 -1.09299300
C -2.87689700 2.11728500 -0.85370500
C -2.78254700 0.81086100 -0.38669800
C -3.95943600 0.08960200 -0.17170400
C -5.21723700 0.61331300 -0.40194900
C -1.56885700 0.03796200 -0.06484100
C -1.85020200 -1.25522000 0.38599900
S -3.59235400 -1.54655800 0.42814100
C -0.25360800 0.45149000 -0.17555300
C 0.78832700 -0.42494700 0.17767900
C 0.47314400 -1.72017000 0.63273100
C -0.84387800 -2.14000300 0.73308300
O -4.07376000 -1.72051600 1.78666800
O -3.98725900 -2.55582800 -0.53779900
N 2.11869100 -0.01270500 0.07939400
C 2.47151900 1.36017100 0.21726600
C 3.32494700 1.95809400 -0.71156900
C 4.31587900 -0.93258300 0.61629100
C 3.16062800 -0.95206000 -0.16688600
C 1.98678500 2.11217900 1.28963700
C 2.34224800 3.44851800 1.42033400
C 3.19670200 4.04444400 0.49609200
C 3.68881900 3.29145700 -0.56624600
C 5.34399900 -1.83281800 0.36375800
C 5.22619600 -2.76711600 -0.66147500
C 4.07209900 -2.78794800 -1.44056500
C 3.04692600 -1.88128100 -1.20293200
H -6.26524600 2.36632800 -1.06294600
H -4.21353600 3.67975100 -1.45706200
H -1.98372000 2.70267400 -1.02921600
H -6.11088600 0.02889600 -0.22426700
H -0.02722100 1.44351700 -0.53832700

H 1.26746700 -2.39513700 0.91640700
H -1.07084100 -3.13614000 1.09111000
H 1.33259400 1.64722500 2.01561700
H 1.96070700 4.02169900 2.25639500
H 3.47759500 5.08445500 0.60437200
H 4.35150300 3.74487400 -1.29311600
H 6.23562500 -1.80948100 0.97820500
H 6.02646600 -3.47075300 -0.85308200
H 3.97348000 -3.50404800 -2.24716200
H 2.15582300 -1.89018000 -1.81702900
H 3.70232200 1.37626700 -1.54249300
H 4.40527900 -0.21125700 1.41818400

5e

SCF energy: -1602.730511 Hartree

Neutral singlet, total number of atoms: 44

C 5.21709100 0.00044700 2.52906400
C 3.99008200 0.00050300 3.19108600
C 2.78993900 0.00034400 2.48435700
C 2.82393700 0.00012200 1.09435700
C 4.06516800 0.00004900 0.45331400
C 5.26633000 0.00021400 1.13639200
C 1.68934200 -0.00001800 0.15517500
C 2.08287300 -0.00019800 -1.18499800
S 3.85895200 -0.00025900 -1.31369900
C 0.33276600 0.00003300 0.45087600
C -0.58586500 -0.00009600 -0.59587900
C -0.17193500 -0.00026400 -1.92614700
C 1.18550700 -0.00032000 -2.23490700
O 4.33658300 1.23790300 -1.89637500
O 4.33646500 -1.23870000 -1.89590100
N -1.98343500 -0.00004000 -0.29956300
C -2.65600600 -1.21070100 -0.08778600
C -4.01980600 -1.18503400 0.24028500
O -4.71672300 0.00011200 0.34507100
C -4.01972500 1.18519200 0.24006600
C -2.65592500 1.21070900 -0.08801200
C -2.02906300 -2.45214700 -0.19314900
C -2.74102600 -3.63135200 0.02237600
C -4.08800800 -3.58847200 0.34931700
C -4.72574500 -2.35258300 0.45889300
C -4.72558800 2.35282800 0.45845300
C -4.08777500 3.58865400 0.34863200
C -2.74079200 3.63138500 0.02167100
C -2.02890600 2.45209400 -0.19363000
H 6.13791100 0.00058300 3.09748200
H 3.96874200 0.00067900 4.27345000
H 1.84343700 0.00039100 3.00902800
H 6.21236600 0.00016500 0.61069300
H -0.01736800 0.00016200 1.47441700
H -0.91491800 -0.00036400 -2.71240900
H 1.51981600 -0.00044900 -3.26410900
H -0.97946600 -2.49844900 -0.44705800
H -2.22866800 -4.58062500 -0.06859700
H -4.64649900 -4.49963300 0.51912800

H -5.77630100 -2.28113700 0.71105900
 H -5.77614900 2.28150000 0.71063300
 H -4.64620800 4.49988100 0.51827100
 H -2.22837200 4.58060600 -0.06949400
 H -0.97931100 2.49827700 -0.44756900

Additional data: HOMO and LUMO energies and MOs primarily involved in the formation of the lowest excited states

PC	HOMO Energy (eV)	LUMO Energy (eV)	Gap (HOMO-LUMO)
4a	-5.84	-1.41	4.43
6a	-5.71	-1.31	4.41
5a	-5.82	-1.76	4.10
5b	-5.76	-1.71	4.06
5c	-5.77	-1.98	3.80
5d	-5.48	-1.84	3.64
5e	-5.06	-2.02	3.04

The most relevant transition involved in the formation of the lowest excited state is provided for each compound; the corresponding coefficients in the CI expansions are also reported; calculations were performed with Time-Dependent DFT, with the employment of the SMD.

PC	Transition for the lowest excited state	Coefficient
4a	HOMO -> LUMO+1	0.70291
6a	HOMO -> LUMO	0.70305
5a	HOMO -> LUMO	0.69329
5b	HOMO -> LUMO	0.50217
5c	HOMO -> LUMO	0.70321
5d	HOMO -> LUMO	0.69693
5e	HOMO -> LUMO	0.70192

Table S7. Most relevant transitions in the D-A photocatalysts.

I. References

1. Ward, J. S.; Nobuyasu, R. S.; Batsanov, A. S.; Data, P.; Monkman, A. P.; Dias, F. B.; Bryce, M. R. *Chem. Commun.*, **2016**, 52, 2612–2615.
2. Hu, M.; Liu, D.; Liu, Y.; Luo, F.; Chen, X.; Yin, Y.; Zhang, S.; Hu, Y. *Adv. Synth. Catal.*, **2024**, 366, 1538–1544.
3. Braveenth, R.; Bae, I. J.; Raagulan, K.; Kim, S.; Kim, S.; Kim, M.; Chai, K. Y.. *Dyes and Pigments*, **2019**, 162, 466–474.
4. Jang, H. J.; Braveenth, R.; Raagulan, K.; Choi, S. Y.; Park, Y. H.; Oh, S. Bin; Bae, I. J.; Kim, B. M.; Wu, Q.; Kim, M.; Chai, K. Y. *Dyes and Pigments*, **2020**, 182, 108697.
5. Sun, N.; Zheng, K.; Zhang, M.; Zheng, G.; Jin, L.; Hu, B.; Shen, Z.; Hu, X. *Green Chemistry*, **2023**, 25, 2782–2789.
6. Zhang, Y.; Yang, Z.; Yang, H.; Li, X.; Yang, L. *Org. Biomol. Chem.*, **2024**, 22, 3381–3385.
7. Emslie, D. J. H.; Blackwell, J. M.; Britten, J. F.; Harrington, L. E. *Organometallics.*, **2006**, 25, 2412–2414.
8. Fu, C.; Luo, S.; Li, Z.; Ai, X.; Pang, Z.; Li, C.; Chen, K.; Zhou, L.; Li, F.; Huang, Y.; Lu, Z. *Chem. Commun.*, **2019**, 55, 6317–6320
9. Fang, M. Y.; Chen, L. P.; Huang, L.; Fang, D. M.; Chen, X. Z.; Wang, B. Q.; Feng, C.; Xiang, S. K. *J. Org. Chem.*, **2021**, 86, 9096–9106.
10. Gan, S.; Luo, W.; He, B.; Chen, L.; Nie, H.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. *Z. J. Mater. Chem. C. Mater.*, **2016**, 4, 3705–3708.
11. Higginbotham, H. F.; Yi, C. L.; Monkman, A. P.; Wong, K. T. *J. Phys. Chem. C.*, **2018**, 122, 7627–7634.
12. Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. *Nat. Prot.*, **2013**, 8, 1535–1550.
13. Romero, N. A.; Nicewicz, D. A. *Chem. Rev.*, **2016**, 116, 10075–10166.
14. Bortolato, T.; Simionato, G.; Vayer, M.; Rosso, C.; Paoloni, L.; Benetti, E. M.; Sartorel, A.; Lebœuf, D.; Dell’Amico, L. *J. Am. Chem. Soc.*, **2023**, 145, 1835–1846.
15. Bryden, M. A.; Millward, F.; Matulaitis, T.; Chen, D.; Villa, M.; Fermi, A.; Cetin, S.; Ceroni, P.; Zysman-Colman, E. *J. Org. Chem.*, **2023**, 88, 6364–6373.
16. Mateos, J.; Rigodanza, F.; Vega-Peñaloza, A.; Sartorel, A.; Natali, M.; Bortolato, T.; Pelosi, G.; Companyó, X.; Bonchio, M.; Dell’Amico, L. *Angew. Chem. Int. Ed.*, **2020**, 59, 1302–1312.
17. Vijayakrishnan, S.; Ward, J. W.; Cooper, A. I. *ACS Catal.*, **2022**, 12, 10057–10064.

J. NMR spectra

