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Supporting Information for:

Tuning BODIPY molecular rotors into the red: sensitivity to viscosity vs temperature

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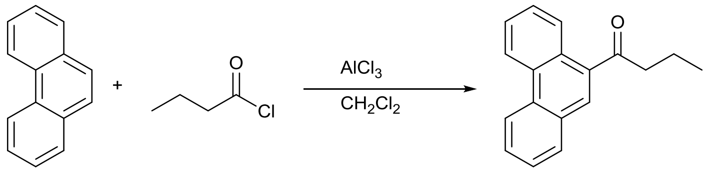
1. Synthesis and NMR characterization details for compounds 2 and 3 and the starting materials

1-(phenanthren-9-yl)butan-1-one

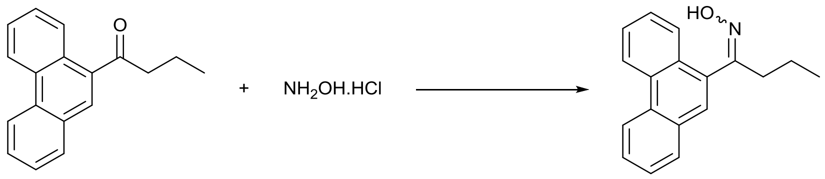


Butyryl chloride (7.94 mL, 0.077 mol) and aluminum trichloride (14.7 g, 0.110 mol) in 30 mL dichloromethane were stirred at 0°C in a round bottom flask. Phenanthrene (12.5 g, 0.070 mol) dissolved in 65 mL of dichloromethane was added dropwise over 40 min. The reaction mixture was brought back to room temperature and stirred for an additional 26 hrs. The reaction mixture was poured onto ice and vigorously stirred until the organic layer became colorless. Diethyl ether was added until the organic layer became less dense than water. The organic layer was separated, washed twice with a saturated $NaHCO_3$ aqueous solution and finally with brine. The organic layer was dried on $MgSO_4$ and the solvents removed under reduced pressure. The crude product was purified by column chromatography on silica (eluent: petroleum ether/toluene 1:2 v/v) to afford 1-(phenanthren-9-yl)butan-1-one (9.1 g, 52%).

NMR: ^1H ($CDCl_3$) δ: 8.70 (d, J=8.2Hz, 1H), 8.52-8.65 (m, 2H), 8.02 (s, 1H), 7.85 (m, 1H), 7.54-7.73 (m, 4H), 3.07 (t, J=6.9 Hz, 2H), 1.87-1.98 (m, 2H), 1.13 (t, J=7.3 Hz, 3H) ppm.

^{13}C ($CDCl_3$) δ: 204.6, 135.3, 131.4, 130.6, 129.8, 129.5, 128.9, 128.4, 128.3, 127.2, 126.9, 126.8, 126.5, 122.7, 122.4, 43.9, 18.0, 13.8 ppm.

1-(phenanthren-9-yl)butan-1-one oxime

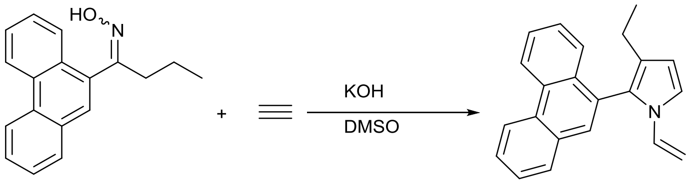


A mixture of 1-(phenanthren-9-yl)butan-1-one (3.10 g, 12.5 mmol) and hydroxylamine hydrochloride (1.08g, 15.6 mmol) in pyridine (40 mL) was heated at 80°C for 16 hrs and then poured into water (100 mL). The crystal precipitates were filtered off, washed with water and dried in vacuo to afford 3.21 g (yield 98%) of the oxime as a white powder.

NMR: ^{1}H ($CDCl_3$) δ: 10.70 (bs, 1H), 8.77 (d, J=7.8Hz, 1H), 8.72 (d, J=8.2Hz, 1H), 8.03 (dd, J=8.0 and 1.1 Hz, 1H), 7-94 (dd, J=7.8 and 1.4 Hz, 1H), 7.76 (s, 1H), 7.62-7.74 (m, 4H), 2.90 (t, J=8.0Hz, 2H), 1.49-1.60 (m, 2H), 0.91 (t, J=7.3Hz, 3H).

^{13}C ($CDCl_3$) δ: 161.3, 133.2, 131.0, 130.6, 130.4, 130.2, 128.9, 127.3, 127.2, 126.8, 126.8, 126.7, 126.1, 123.0, 122.5, 32.1, 19.2, 14.3 ppm.

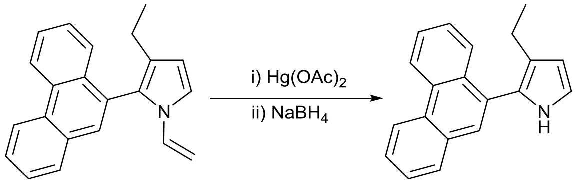
3-ethyl-2-(phenanthren-9-yl)-1-vinylpyrrole



A mixture of 1-(phenanthren-9-yl)butan-1-one oxime (2.50 g, 9.5 mmol) and KOH (0.66 g, 11.9 mmol) in DMSO (100 mL) was heated at 100°C and acetylene gas was passed through for 2 hrs. The reaction mixture was brought back to room temperature and diluted with water (150 mL), and extracted with diethyl ether (6 × 50 mL). The extracts were washed with water (3 × 50 mL) and dried over $MgSO_4$. The residue, obtained after evaporation of the diethyl ether in vacuo, was purified by column chromatography on alumina (eluent, petroleum ether/diethyl ether 3:1 v/v). 3-ethyl-2-(phenanthren-9-yl)-1-vinylpyrrole was isolated in 25% yield (0.71g) with traces amounts of the corresponding pyrrole.

NMR: ^{1}H ($CDCl_3$) δ: 8.71-8.77 (m, 2H), 7.91 (dd, J=7.8 and 1.4 Hz, 1H), 7.74 (s, 1H), 7.61-7.73 (m, 3H), 7.51-7.56 (m, 2H), 7.20 (d, J=2.8, 1H), 6.32-6.43 (m, 2H), 5.00 (dd, J=15.8 and 1.1 Hz, 1H), 4.33 (dd, J=8.9 and 1.1 Hz, 1H), 2.29 (q, J=7.8 Hz, 2H), 1.05 (t, J=7.8 Hz, 2H) ppm.

3-ethyl-2-(phenanthren-9-yl)pyrrole

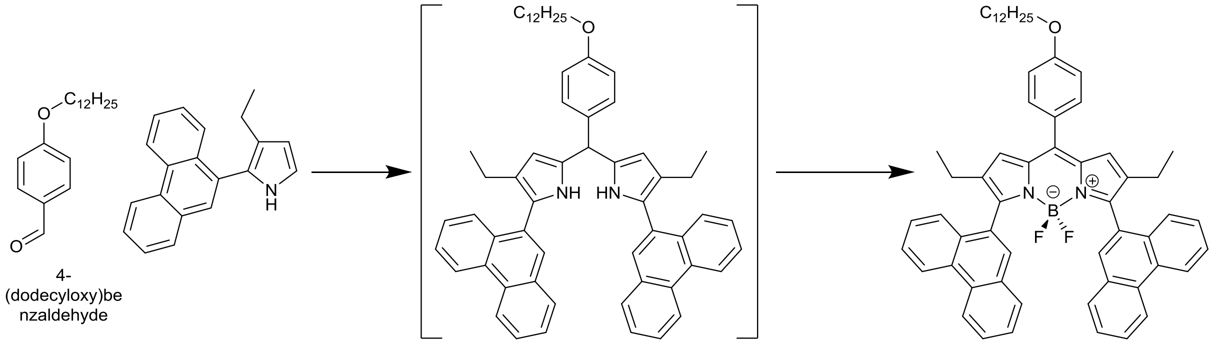


Mercury acetate (2.25 g, 7.1 mmol) in 10% aqueous acetonitrile (25 mL) was added to 3-ethyl-2-(phenanthren-9-yl)-1-vinylpyrrole (0.70 g, 2.4 mmol) in acetonitrile (25 mL) while stirring. The reaction mixture was stirred for 30 min at 50°C, then sodium borohydride (0.33 g, 8.7 mmol) was added in small portions. After gas evolution was complete, the residue was filtered off. The filtrate was diluted with brine (50 mL), extracted with diethyl ether (3×15 mL), and the combined ether extracts were dried over K_2CO_3. Diethyl ether was removed and the crude product was purified by column chromatography on alumina (eluent, petroleum ether/diethyl ether 4:1 v/v). 3-ethyl-2-

(phenanthren-9-yl)pyrrole was isolated in 39% yield (0.25g)

NMR: ^{1}H (CDCl$_3$) δ: 8.68-8.77 (m, 2H), 8.11 (bs, 1H), 7.84-7.90 (m, 2H), 7.74 (s, 1H), 7.52-7.71 (m, 4H), 6.90 (s, 1H), 6.33 (s, 1H), 2.45 (q, J=7.5 Hz, 2H), 1.14 (t, J=7.5 Hz, 3H) ppm.

Bodipy 2:

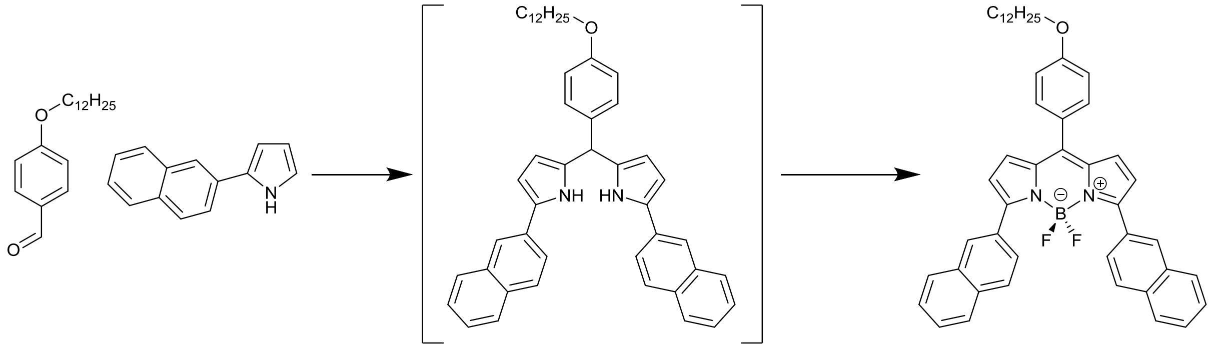


3-ethyl-2-(phenanthren-9-yl)pyrrole (0.10 g, 0.37 mmol) and 4-(dodecyloxy)benzaldehyde[i] (0.054 g, 0.18 mmol) were dissolved in dichloromethane (25 mL) in a one neck round bottom flask and flushed with nitrogen. Then two drops of TFA were added and the obtained solution was stirred for 23 h under nitrogen at room temperature. Then chloranil (0.045 g, 0.18 mmol) was added and the reaction mixture was stirred for 10 min. Diisopropylethylamine (0.23 mL, 1.29 mmol) was added dropwise to the mixture and immediately after boron trifluoride etherate (0.25 mL, 2.03 mmol) was added and the reaction mixture was stirred for 0.5 h. After evaporation of the solvent in vacuo, chromatography was performed on the crude product on silica gel (eluent CH_2Cl_2/petroleum ether=1:3 to 1:2 v:v) to afford BODIPY **2** (0.052 g, 33%).

NMR ^{1}H (CDCl$_3$) δ : 8.57-8.65 (m, 4H), 7.89 (d, 2H, J=XX Hz), 7.69-7.74 (m, 4H), 7.40-7.62 (m, 10H), 7.14 (d, J=xxHz, H phényl), 6.85 (s, 2H, H pyrrole), 4.12 (t, J=6.6Hz, 2H, O-$\mathit{CH_2}$); 1.91-2.22 (m, 4H, $\mathit{CH_2}$-CH_3), 1.87 (m, 2H, H_{11}), 1.52 (m, 2H, H_{10}), 1.26-1.34 (m, 16H, H_2-H_9), 0.90 (m, 6H; CH_2-$\mathit{CH_3}$), 0.86 (t, 3H, J=6.6 Hz, H_1 $\mathit{CH_3}$) ppm.

^{13}C (CDCl$_3$) δ : 161.0 (Cq), 155.0 (Cq), 137.2 (Cq), 134.5 (Cq), 132.3 (CH), 131.0 (Cq), 130.9 (Cq), 130.6 (Cq), 130.1 (Cq), 129.7 (CH), 129.7 (CH), 129.5 (CH), 128.5 (Cq), 127.1 (CH), 126.9 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 124.5 (Cq), 122.8 (CH), 122.5 (CH), 121.4 (Cq), 114.4 (CH), 68.4 (O-CH_2), 32.0 (CH_2), 29.6-29.9 (several CH_2), 29.4 (CH_2), 26.2 (CH_2), 22.8 (CH_2), 19.2 (CH_2), 14.3 (CH_3), 14.2 (CH_3) ppm.

Bodipy 3:



2-(naphthalen-2-yl)-pyrrole[ii] (0.10 g, 0.52 mmol) and 4-(dodecyloxy)benzaldehyde (0.075 g, 0.26 mmol) were dissolved in dichloromethane (25 mL) in a one neck round bottom flask and flushed with nitrogen. Then three drops of TFA were added and the obtained solution was stirred for 23 h under nitrogen at room temperature. Then chloranil (0.064 g, 0.26 mmol) was added and the reaction mixture was stirred for 10 min. Diisopropylethylamine (0.32 mL, 1.81 mmol) was added dropwise to the mixture and immediately after boron trifluoride etherate (0.35 mL, 2.85 mmol) was added and the reaction mixture was stirred for 0.5 h. After evaporation of the solvent in vacuo, chromatography was performed on the crude product on silica gel (eluent CH_2Cl_2/petroleum ether=1:3 to 1:2 v:v) to afford BODIPY **3** (0.06 g, 36%).

NMR ^1H ($CDCl_3$) δ : 8.36 (s, 2H, H_{23}), 8.01 (d, 2H, J=8.7Hz, H_{25}), 7.81-7.90 (m, 6H), 7.59 (d, 2H, J=8.7 Hz, H_{15}), 7.44-7.51 (m, 4H), 7.07 (d, 2H, J=8.2 Hz, H_{14}), 7.01 (d, 2H, J=4.1 Hz, H_{19}), 6.77 (d, 2H, J=4.1 Hz, H_{20}), 4.08 (t, 2H, J=6.6 Hz, H_{12}), 1.87 (m, 2H, H_{11}), 1.52 (m, 2H, H_{10}), 1.26-1.34 (m, 16H, H_2-H_9), 0.90 (t, 3H, J=6.6 Hz, H_1) ppm.

^{13}C ($CDCl_3$) δ : 161.3 (Cq), 158.4 (Cq), 144.3 (Cq), 136.8 (Cq), 133.7 (Cq), 133.1 (Cq), 132.6 (C_{15}), 130.9 (C_{19}), 130.3 (Cq), 129.5 (C_{23}), 129.1 (CH), 127.9 (CH), 127.7 (CH), 127.0 (CH), 126.9 (C_{25}), 126.8 (Cq), 126.3 (CH), 121.2 (C_{20}), 114.5 (C_{14}), 68.4 (C_{12}), 32.1 (CH_2), 29.5-29.8 (several CH_2), 29.3 (C_{11}), 26.2 (C_{10}), 22.8 (CH_2), 14.3 (C_1) ppm.

2. Additional spectroscopic data

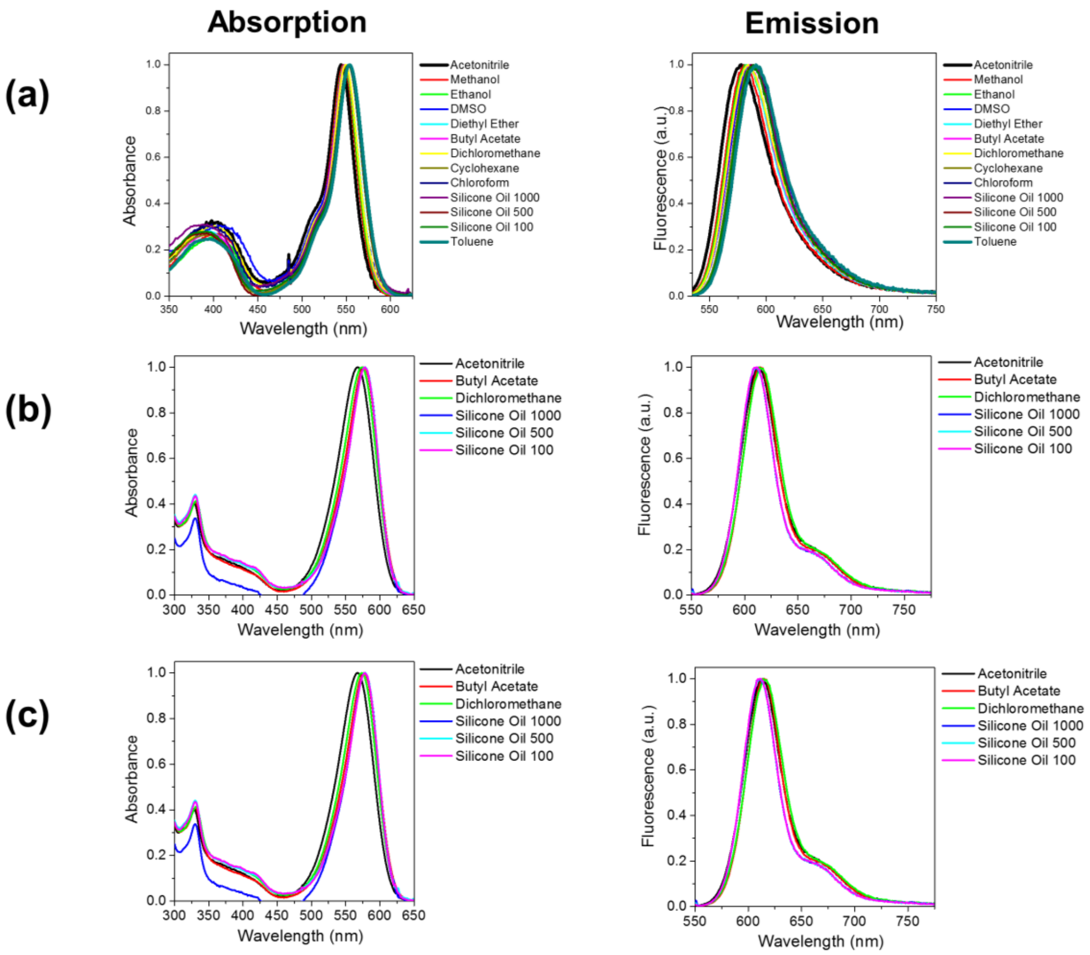


Figure S1. Normalized absorption (left) and fluorescence (right) spectra of compounds **2** (a), **3** (b) and **4** (c) in different solvents

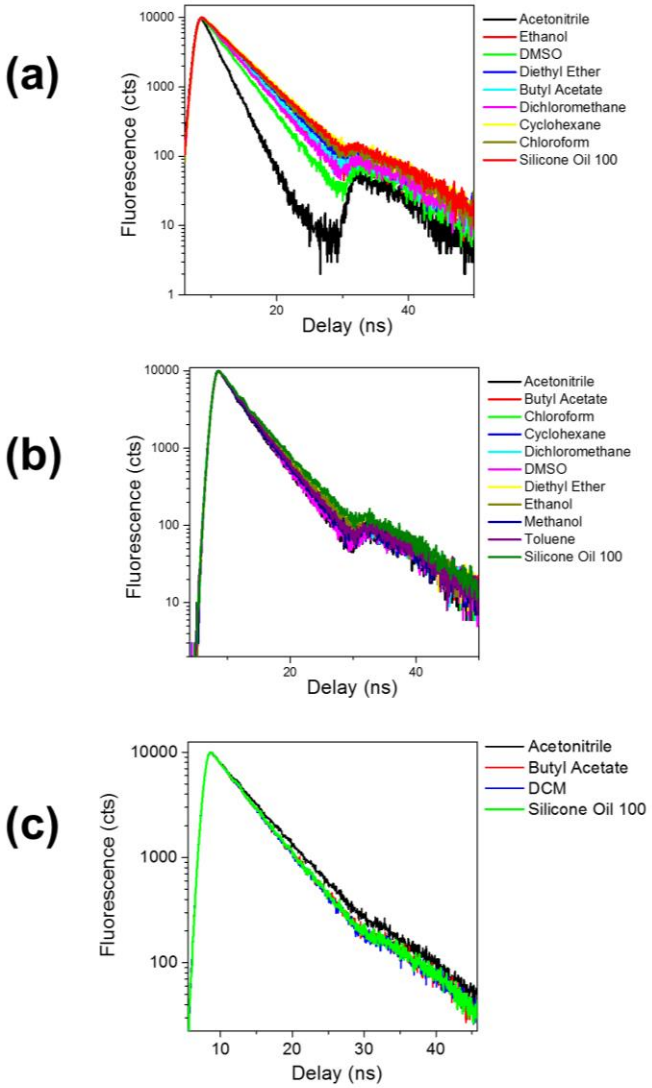


Figure S2. Time resolved fluorescence decays recorded for compounds **2** (a), **3** (b) and **4** (c) in different solvents.

Table S1. Spectroscopic properties of compound **2** in different solvents: absorption ($\lambda_{max, abs}$) and emission ($\lambda_{max, fluo}$) maximum wavelength, Stokes shift ($D_{Stokes)}$), fluorescence lifetime (τ_{fluo}) and fluorescence quantum yield (Φ_{fluo}), radiative (k_r) and non radiative (k_{nr}) rate constants.

Solvent	**$\lambda_{max, abs}$ (nm)**	**$\lambda_{max, fluo}$ (nm)**	**D_{Stokes} (cm^{-1})**	**τ_{fluo} (ns)**	**χ^2**	**Φ_{fluo}**	**$k_r \times 10^8$ (s^{-1})**	**$k_{nr} \times 10^8$ (s^{-1})**
Acetonitrile	544	577	1051	2.21	1.15	0.33	1.47	3.05
Methanol	547	581	1070	3.24	1.25	0.51	1.57	1.51
DMSO	548	587	1212	3.48	1.15	0.57	1.63	1.24
Dichloromethane	549	584	1092	3.91	1.29	0.66	1.69	0.87
Ethanol	548	584	1125	4	1.27	0.66	1.65	0.85
Toluene	554	591	1130	4.03	1.14	0.75	1.87	0.61
Butyl Acetate	549	585	1121	4.11	1.18	0.70	1.71	0.73
Diethyl Ether	549	584	1092	4.39	1.23	0.71	1.63	0.65
Chloroform	553	588	1076	4.54	1.18	0.76	1.67	0.53
Silicone Oil 100	553	589	1105	4.61	1.33	0.72	1.56	0.61
Silicone Oil 500	553	587	1047	4.62	1.27	0.75	1.62	0.54
Silicone Oil 1000	552	588	1109	4.67	1.38	0.73	1.55	0.59
Cyclohexane	552	587	1080	4.81	1.24	0.83	1.73	0.35

Table S2. Spectroscopic properties of compound **3** in different solvents: absorption ($\lambda_{max, abs}$) and emission ($\lambda_{max, fluo}$) maximum wavelength, Stokes shift ($D_{Stokes)}$) and fluorescence quantum yield (Φ_{fluo}).

Solvent	**$\lambda_{max, abs}$ (nm)**	**$\lambda_{max, fluo}$ (nm)**	**D_{Stokes} (cm^{-1})**	**Φ_{fluo}**
Cyclohexane	571	608	1065.8	0.69
Toluene	575	615	1131.1	0.77
Diethyl Ether	568	609	1185.3	0.66
Butyl acetate	570	612	1204.0	0.70
Chloroform	571	612	1173.3	0.71
Dichloromethane	568	612	1265.8	0.66
Ethanol	575	611	1024.7	0.64
Methanol	566	609	1247.5	0.56
Acetonitrile	561	610	1431.9	0.53
DMSO	572	621	1379.5	0.61
Silicone Oil 1000	573	607	977.5	0.77
Silicone Oil 500	573	607	977.5	0.77
Silicone Oil 100	573	607	977.5	0.76

Table S3. Fluorescence quantum yield (Φ_{fluo}) recorded for compound **4** in different solvents.

Solvent	Φ_{fluo}
Butyl acetate	0.93
Dichloromethane	0.86
Acetonitrile	1.00
Silicone Oil 1000	0.90
Silicone Oil 500	0.83
Silicone Oil 100	0.94

Table S4. SdP parameters[iii] for solvents used in Figure 7, main text.

Solvent	**SdP parameter**[iii]
Acetonitrile	0.974
Methanol	0.904
DMSO	1.0
Dichloromethane	0.769
Ethanol	0.783
Toluene	0.284
Butyl Acetate	0.535
Diethyl Ether	0.385
Chloroform	0.614
Cyclohexane	0.0

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[i] Brun, A.; Etemad-Moghadam, G. *Synthesis*, **2002**, 1385-1390.

[ii] Schmidt, E.Y.; Zorina, N. V.; Dvorko, M. Y.. Protsuk, N. I.; Belyaeva, K. V.; Clavier, G.; Méallet-Renault, R.; Vu, T. T.; Mikhaleva A. I; Trofimov B. A. *Chemistry –Eur. J.*, **2011**, *17*, 3069-3073.

[iii] J. Catalán, *J. Phys. Chem. B*, **2009**, *113* (17), pp 5951–5960