Supplementary material for manuscript:

Photon-induced intramolecular charge transfer with the influence of D/A group and mode: Optical physical properties and bio-imaging

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Synthesis and characterizations

The target compounds, **a1-a5** and **b1-b4** have been prepared according to synthetic routes shown in **Scheme 1**. The experimental details are introduced as follows:

Preparation of 4-Diphenylaminobenzaldehyde (M1): 4-Diphenylaminobenzaldehyde (**M1**) was prepared referring the literature. [8]

Preparation of 4, 4-diformyl triphenylamine (M2): 4, 4-diformyl triphenylamine (**M2**) was prepared referring the literature. [7]

Preparation of 4-[N, N'-bis(4-ethoxyphenyl)amino]benzaldehyde (M3): 4-[N, N'-bis(4-ethoxyphenyl)amino] benzaldehyde (**M3**) was prepared referring the literature. [8]

Preparation of 4-(1H-pyrazol-1-yl) benzaldehyde (M4): 4-[N, N'-bis(4-ethoxyphenyl)amino] benzaldehyde (**M4**) was prepared referring the literature. [9]

Preparation of 4-(1H-imidazole1-yl) benzaldehyde (M5): 4-[N, N'-bis(4-ethoxyphenyl)amino] benzaldehyde (**M3**) was prepared referring the literature. [9]

Preparation of a1: M1 (2.7 g, 10 mmol) was dissolved in 50 mL of ethanol. 1, 2-diaminobenzene (1.1 g, 10 mmol) was added. The stirred mixture was refluxed at 80 $^{\circ}$C for 8h, and the resulting precipitation was filtered and recrystallization with ethanol to afford the product as pale-yellow solid. Yield: 2.2 g (67 %). ^{1}H-NMR (400 MHz, d_6-DMSO): δ = 12.72 (1H, s), 8.04-8.06 (2H, d, J = 8.4 Hz), 7.60-7.62 (1H, d, J = 7.2 Hz) 7.47-7.49 (1H, d, J = 7.2 Hz), 7.35-7.39 (4H, d, J = 7.8 Hz), 7.11-7.12 (8H, m), 6.92-6.94 (2H, d, J = 8.4Hz). ^{13}C-NMR (100 MHz, d_6-DMSO): 151.2, 148.7, 146.6, 129.7, 129.5, 127.6, 124.9, 123.9, 123.4, 121.6. IR (KBr, cm^{-1}) 3446, 3056, 2919, 2853, 1592, 1493, 1478, 1436, 1402, 1331, 1275, 1193, 1118, 1076, 968, 841, 748, 695, 618, 509.

MALDI-TOF m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}N_3$ 362.166; Found 362.171

Preparation of a2: M3 (3.6 g, 10 mmol) was dissolved in 50 mL of ethanol. 1, 2-diaminobenzene (1.1 g, 10 mmol) was added. The stirred mixture was refluxed at 80 °C for 8h, and the mixture was evaporated. The residue was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (5/1, v/v) as eluent to afford the product as pale-yellow solid. Yield: 2.0 g (43 %) ^{1}H-NMR (400 MHz, d_6-DMSO): δ = 12.69 (1H, s), 7.93-7.95 (2H, d, J = 8.4 Hz), 7.52 (2H, s), 7.10-7.12 (6H, m), 6.94-6.96 (4H, d, J = 8.4 Hz), 6.80-6.82 (2H, d, J = 8.4 Hz), 4.00-4.05 (4H, q, J = 6.9 Hz), 1.32-1.35 (6H, d, J = 7Hz). ^{13}C-NMR (100 MHz, d_6-DMSO): δ = 155.6, 151.6, 149.8, 139.1, 127.5, 127.4, 126.5, 121.5, 120.9, 117.6, 115.5, 63.2, 14.7. IR 3445, 3061, 2924, 2853, 1592, 1489, 1448, 1332, 1287, 1190, 838, 807, 754, 696, 510. IR (KBr, cm^{-1}) 3445, 3042, 2975, 2925, 1604, 1506, 1472, 1440, 1396, 1319, 1274, 1238, 1192, 1165, 1113, 1046, 827, 746, 523. MALDI-TOF m/z: $[M +H]^+$ Calcd for $C_{29}H_{28}N_3O_2$ 450.218; Found 450.218

Preparation of a3: M1 (2.7 g, 10 mmol) was dissolved in 50 mL of nitrobenzene. 3, 3'-Diaminobenzidine (1.1 g, 5 mmol) was added. The stirred mixture was refluxed at 130 °C for 24h, and the resulting precipitation was filtered, washed with ethanol-CH_2Cl_2 (1/1,v/v) and dried to afford the product as yellow solid. Yield: 2.6 g (68 %). ^{1}H-NMR (400 MHz, d_6-DMSO): δ = 12.80 (2H, s), 8.07-8.10 (4H, d, J = 8.8 Hz), 7.80 (2H, s), 7.63 (2H, s), 7.51-7.53 (2H, d, J = 8.4 Hz), 7.36-7.40 (8H, t, J = 7.8 Hz), 7.12-7.16 (12H, t, J = 7.6 Hz), 7.06-7.08 (4H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, d_6-DMSO): δ = 151.9, 148.8, 146.6, 129.8, 127.6, 124.9, 123.9, 123.2, 121.6. IR 3445, 3061, 2924, 2853, 1592, 1489, 1448, 1332, 1287, 1190, 838, 807, 754, 696, 510. MALDI-TOF m/z: $[M + H]^+$ Calcd for $C_{50}H_{37}N_6$ 721.308; Found 721.307.

Preparation of a4: M3 (3.6 g, 10 mmol) was dissolved in 50 mL of nitrobenzene. 3,

3'-Diaminobenzidine (1.1 g, 5 mmol) was added. The stirred mixture was refluxed at 130 °C for 24h, and the resulting precipitation was filtered, washed with ethanol and dried to afford the product as yellow solid. Yield: 2.78 g (59 %). ^{1}H-NMR (400 MHz, d_6-DMSO): δ = 12.68 (2H, s), 7.97-7.99 (4H, d, J = 8.8 Hz), 7.84 (1H, s), 7.66 (2H, m), 7.46-7.54 (3H, m), 7.11-7.13 (8H, d, J = 8.8 Hz), 6.94-6.97 (8H, d, J = 8.4 Hz), 6.81-6.83 (4H, d, J = 8.8 Hz), 4.00-4.05 (8H, q, J = 6.9 Hz), 1.32-1.35 (12H, t, J = 6.8 Hz). ^{13}C-NMR (100 MHz, d_6-DMSO): δ = 156.5, 152.5, 149.6, 137.7, 136.7, 129.1, 128.3, 115.9, 115.7, 63.3, 14.65. IR (KBr, cm^{-1}) 3446, 2924, 2854, 1607, 1505, 1477, 1461, 1392, 1320, 1282, 1238, 1191, 1166, 1113, 1045, 826, 803, 697, 603, 577, 526. MALDI-TOF m/z: $[M+H]^+$ Calcd for $C_{50}H_{37}N_6$ 897.413; Found 897.071.

Preparation of a5: M2 (3.0 g, 10 mmol) was dissolved in 50 mL of nitrobenzene. 1, 2-diaminobenzene (2.2 g, 20 mmol) was added. The stirred mixture was refluxed at 100 °C for 24h, and the resulting precipitation was filtered and washed with CH_2Cl_2 to afford the product as yellow solid. Yield: 3.6 g (69 %). ^{1}H-NMR (400 MHz, d_6-DMSO): δ = 12.83 (2H, s), 8.12-8.14 (4H, d, J = 8.8 Hz), 7.57 (4H, s), 7.41-7.45 (2H, t, J = 7.8 Hz), 7.17-7.21 (11H, m). ^{13}C-NMR (100 MHz, d_6-DMSO): δ = 151.0, 148.1, 146.2, 130.0, 127.8, 125.6, 124.6, 124.4, 123.2, 121.9. IR (KBr, cm^{-1}) 3446, 2958, 2920, 2853, 1603, 1494, 1477, 1438, 1429, 1399, 1318, 1276, 1180, 1120, 874, 840, 746, 698, 613, 551, 513. MALDI-TOF m/z: $[M]^+$ Calcd for $C_{32}H_{23}N_5$ 447.203; Found 447.129.

Preparation of b1: M4 (1.7 g, 10 mmol) was dissolved in 50 mL of ethanol. 1, 2-diaminobenzene (1.1 g, 10 mmol) was added. The stirred mixture was refluxed at 80 °C for 8h, and the resulting precipitation was filtered and recrystallization with ethanol to afford the product as pale-yellow solid. Yield: 2.3 g (82 %). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ = 12.94 (s, 1H), 8.62-8.63 (d,

1H, J = 2.4 Hz), 8.29-8.31 (d, 2H, J = 8.4 Hz), 8.04-8.06 (d, 2H, J = 8.8 Hz), 7.81-7.82 (d, 1H, J = 2.4 Hz), 7.67-7.69 (d, 1H, J = 7.8 Hz), 7.54-7.56 (d, 1H, J = 7.8 Hz), 7.18-7.25 (m, 2H), 6.60-6.61(t, 1H, J = 4.0 Hz), ^{13}C-NMR (DMSO-d_6, 100 MHz, TMS): δ = 150. 6, 143.8, 141.4, 140.5, 135.0, 127.9, 127.8, 127.7, 122.5, 121.6, 118.8, 118.5, 111.3, 108.2. IR (KBr, cm^{-1}) 3440.70, 3062.63, 2859.94, 2760.50, 2668.06, 1613.06, 1520.11, 1504.67, 1479.13, 1445.41, 1421.75, 1391.88, 1337.57, 1317.72, 1275.69, 1228.85, 1201.08, 1127.26, 1070.71, 1048.35, 1031.14, 1005.47, 968.65, 936.02, 915.09, 846.11, 750.39, 736.69, 609.91, 517.78. MALDI-TOF m/z: [M + H]$^+$ Calcd for $C_{16}H_{13}N_4$ 260.106; Found 261.092.

Preparation of b2: M5 (1.7 g, 10 mmol) was dissolved in 50 mL of ethanol. 1, 2-diaminobenzene (1.1 g, 10 mmol) was added. The stirred mixture was refluxed at 80 °C for 8h, and the resulting precipitation was filtered and recrystallization with ethanol to afford the product as pale-yellow solid. Yield: 2.3 g (82 %). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ = 12.97 (s, 1H), 8.40 (s, 1H), 8.29-8.31 (d, 2H, J = 8.8 Hz), 7.89 (s, 1H), 7.87-7.88 (d, 2H, J = 1.2 Hz), 7.67-7.69 (d, 1H, J = 7.6 Hz), 7.54-7.56 (d, 1H, J = 7.8 Hz), 7.20-7.24 (m, 2H), 7.16 (s, 1H), ^{13}C-NMR (DMSO-d_6, 100 MHz, TMS): δ = 150.3, 143.8, 137.7, 135.5, 135.0, 130.1, 128.4, 127.8, 122.6, 121.8, 120.4, 118.9, 117.8, 111.3. IR (KBr, cm^{-1}) 3447.82, 3108.73, 1608, 1550.02, 1507.54, 1438.64, 1311.13, 1276.89, 1248.26, 1119.47, 1060.30, 963.94, 841.19, 739.96, 654.49, 526.23. MALDI-TOF m/z: [M]$^+$ Calcd for $C_{32}H_{23}N_5$ 260.106; Found 261.100.

Preparation of b3: M4 (1.7 g, 10 mmol) was dissolved in 50 mL of nitrobenzene. 3, 3'-Diaminobenzidine (1.1 g, 5 mmol) was added. The stirred mixture was refluxed at 130 °C for 24h, and the resulting precipitation was filtered and washed with CH_2Cl_2 to afford the product as yellow solid. Yield: 2.3 g (82 %). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ = 13.05 (s, 2H),

8.65-8.65 (d, 2H, *J* = 2.4 Hz), 8.34-8.36 (d, 4H, *J* = 8.8 Hz), 8.07-8.10 (d, 4H, *J* = 8.8 Hz), 7.89 (s, 2H) 7.82-7.83 (d, 2H, *J* = 1.6 Hz), 7.68-7.73 (d, 2H, *J* = 7.8 Hz), 7.60-7.62 (d, 2H, *J* = 8.4 Hz), 6.62-6.63 (t, 2H, *J* = 2.0 Hz), ^{13}C-NMR (DMSO-d_6, 100 MHz, TMS): δ = 151.2, 141.4, 140.5, 135.9, 135.2, 135.1, 129.7, 127.8, 127.7, 123.2, 122.1, 118.6, 108.2. IR (KBr, cm^{-1}) 3364.93, 3099.98, 1613.13, 1551.57, 1519.90, 1497.98, 1469.39, 1448.56, 1469.39, 1448.56, 1420.42, 1395.67, 1338.42, 1294.80, 1201.98, 1125.88, 1051.03, 939.49, 844.90, 800.24, 751.20, 654.98, 612.96, 539.79. MALDI-TOF m/z: $[M]^+$ Calcd for $C_{32}H_{22}N_8$ 519.197; Found 519.203.

Preparation of b4: M5 (1.7 g, 10 mmol) was dissolved in 50 mL of nitrobenzene. 1, 2-diaminobenzene (1.1 g, 5 mmol) was added. The stirred mixture was refluxed at 130 °C for 24h, and the resulting precipitation was filtered and washed with CH_2Cl_2 to afford the product as yellow solid. Yield: 2.3 g (82 %). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ = 13.06 (s, 2H), 8.43(s, 2H), 8.33-8.36 (d, 4H, *J* = 8.4 Hz), 7.89-7.91 (d, 8H, *J* = 8.6 Hz), 7.69-7.70 (m, 2H), 7.59-7.60 (d, 2H, *J* = 7.8 Hz), 7.2 (s, 2H). The ^{13}C-NMR of **b4** can hardly get due to its poor solubility. IR (KBr, cm^{-1}) 3340.34, 3106.78, 1606.36, 1552.10, 1508.17, 1436.38, 1389.00, 1306.90, 1249.55, 1177.12, 1118.65, 1060.59, 962.35, 952.13, 914.77, 835.91, 800.62, 737.23, 691.41, 650.57, 617.83, 531.06. MALDI-TOF m/z: $[M]^+$ Calcd for $C_{32}H_{22}N_8$ 519.197; Found 519.201.

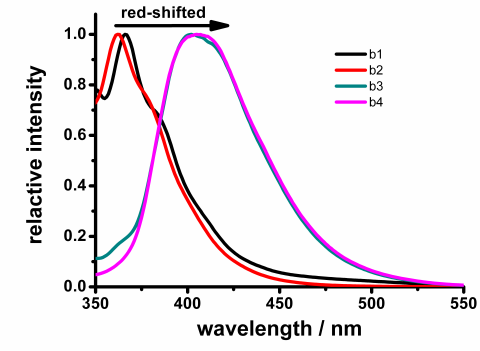
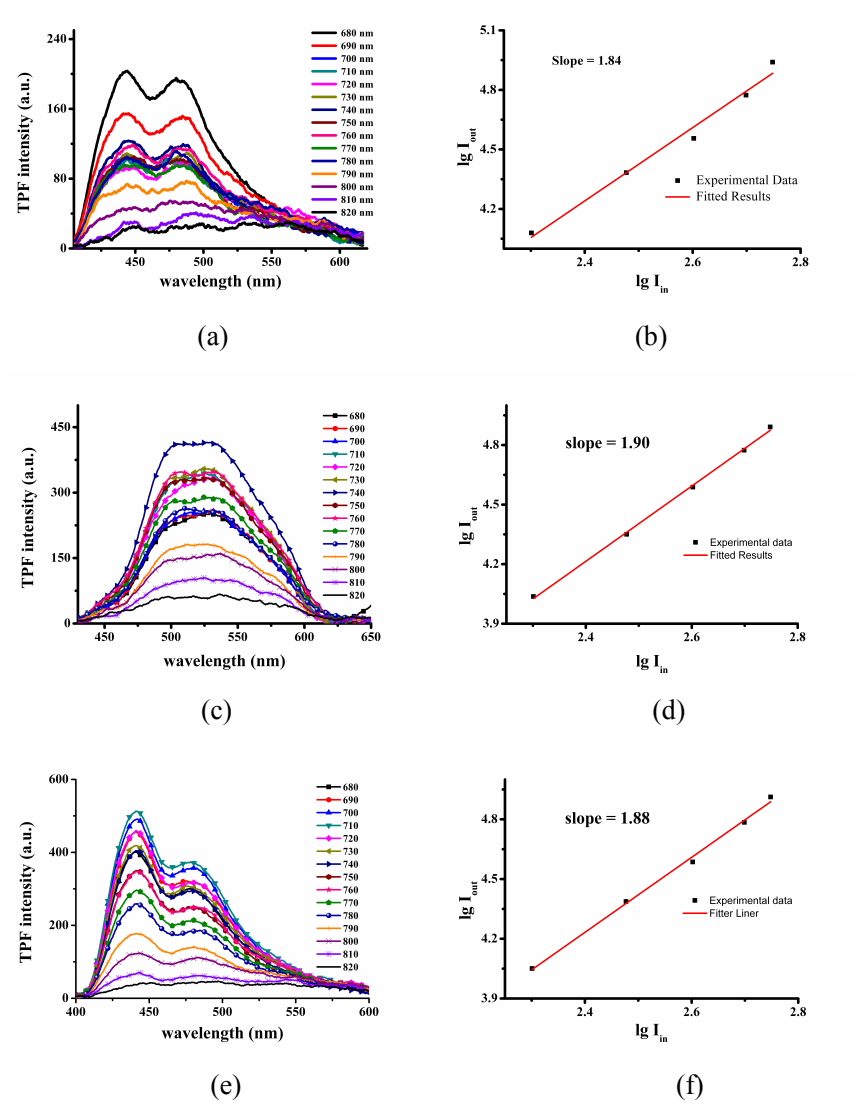
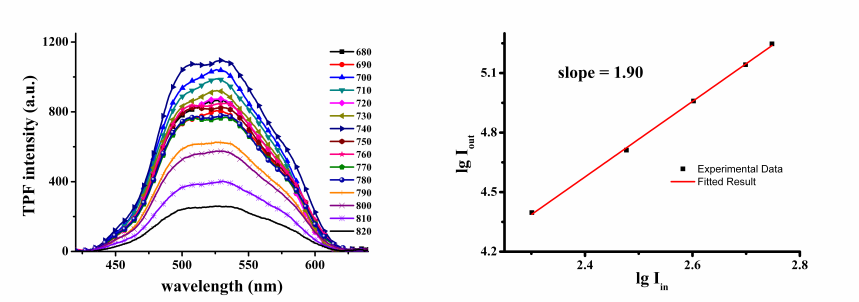


Figure S1. Normalized one-photon emission spectra of **b1-b4** in DMF





(g) (h)

Figure S2. the TPEF spectra of (a) **a1** (c) **a2** (e) **a3** (g) **a4** in DMF pumped by femtosecond laser pulses at 400 mw under different excitation wavelengths, respectively. Output fluorescence(I_{out}) vs. the square of input laser power (I_{in}) for (b) **a1** in different powers under 680 nm (d) **a2** in different powers under 740 nm (f) **a3** in different powers under 710 nm (h) **a4** in different powers under 740 nm, respectively.

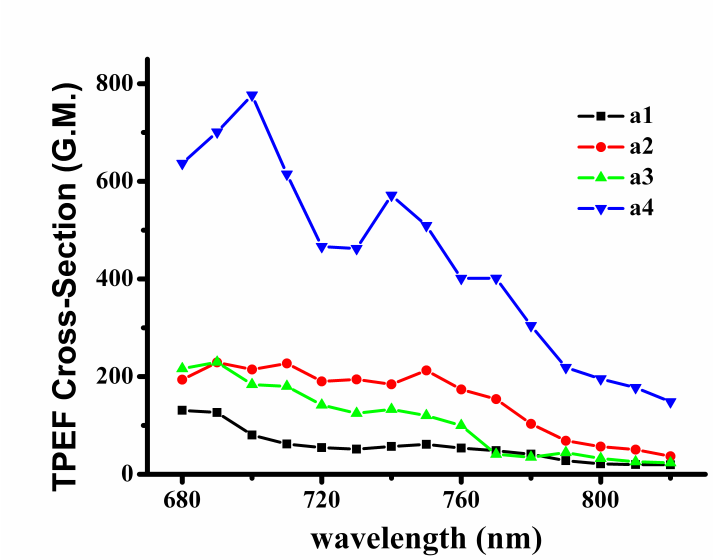


Figure S3. Two-photon absorption cross-sections of **a1**-**a5** in 680-820nm regions.

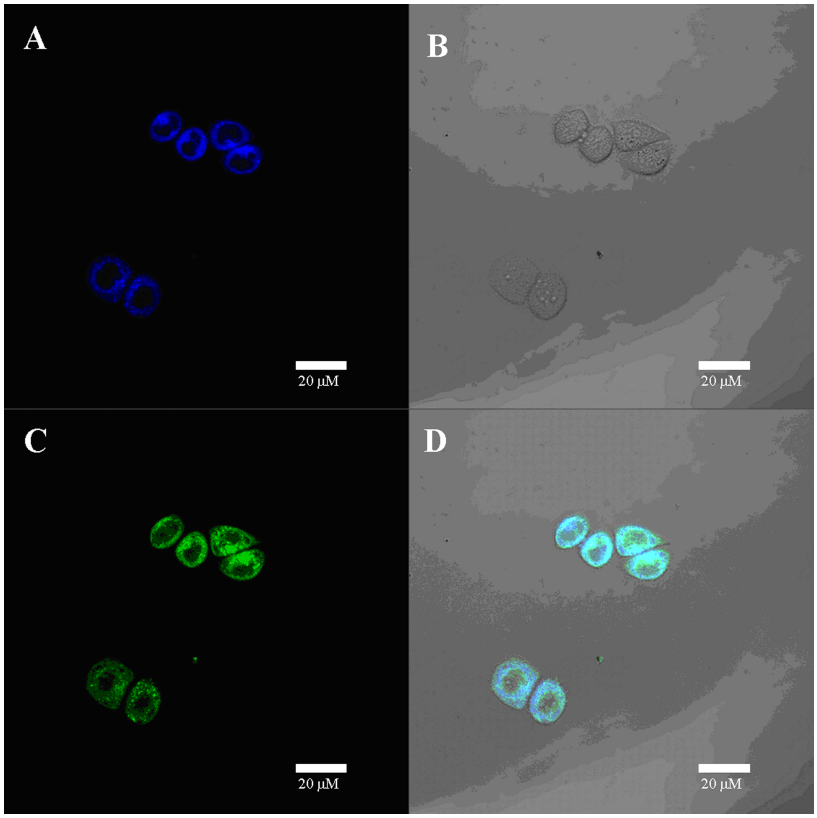


Figure S4. (A) One-photon fluorescence microscopy (OPFM) image of HepG2 cells with excitation at 350 nm (B) Bright-field image of HepG2 cells stained with **a1**. (C) Two-photon fluorescence microscopy (TPFM) image of HepG2 cells with excitation at 680 nm. (D) Merged image.

Table S1. The λ_{abs}, λ_{em} and stock shifts with **a1-a5** in different solvents

	solvents	λ_{abs} [a]	λ_{em} [c]	stock shifts [d]
a1	benzene	353	401	3391
	ethyl acetate	346	408	4309
	DMF	351	424	4905
	DMSO	354	432	5100
a2	benzene	354	448	5927
	ethyl acetate	348	458	7020
	DMF	350	477	7607
	DMSO	354	488	7757
a3	benzene	374	409	2288
	ethyl acetate	368	406	2543
	DMF	374	416	2700
	DMSO	376	421	2843
a4	benzene	379	444	3863
	ethyl acetate	368	452	5050
	DMF	374	478	5817
	DMSO	378	489	6005
a5	benzene	373	408	2300
	ethyl acetate	365	407	2827
	DMF	372	419	3015
	DMSO	373	426	3335
b1	benzene	320	367	4002
	ethyl acetate	317.5	363	3948
	DMF	319	366	4026
	methanol	320	369	4150
	DMSO	320	367	4002
b2	benzene	315	361	4045
	ethyl acetate	311	358	4221
	DMF	314	362	4223
	DMSO	317	369	4445
b3	benzene	344.5	395	3711
	ethyl acetate	342.5	394	3816
	DMF	347	402	3943
	DMSO	349	404	3901
b4	benzene	342.5	396	3945
	ethyl acetate	377	395	1209
	DMF	340.5	405	4677
	DMSO	344	407	4500

[a] Absorption peak position in nm (1 μM). [b] Peak position of OPEF in nm (1 μM), excited at the absorption maximum. [c] Stokes shift in cm^{-1}.