Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Deep-blue-emitting nanoaggregates from carbazole-based dyes in water

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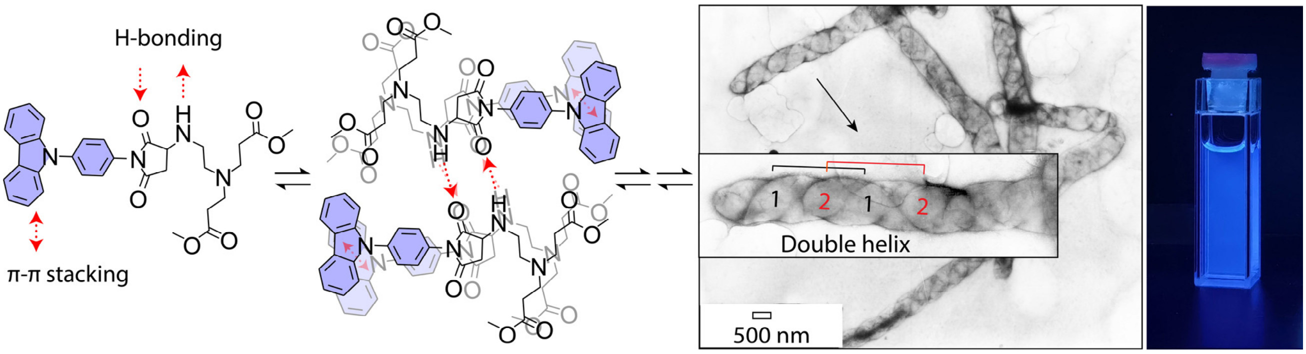

Amphiphilic carbazole-based dyes assemble in water into deep-blue-emitting helical nanoaggregates by self-complementary, antiparallel H-bonding and π-π stacking interactions.

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1. Materials and measurements

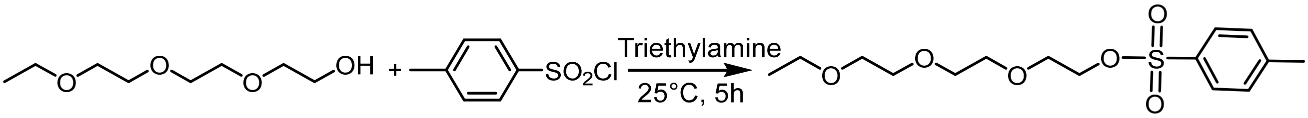
^{1}H NMR, ^{13}C NMR spectra were measured on a Bruker (400 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Mettler ReaTIR45 in FTIR spectrometer. High resolution mass spectra (HRMS) were obtained on a Bruker miorOTOF-QII using ESI. Elemental analysis was obtained on the Vario EL CUBE elemental analyzer from Elementar Analysen system GmbH. UV-vis absorption spectra were measured on an Agilent Varian Cary 300 spectrometer. Steady-state fluorescence spectra were recorded on an Edinburgh Instruments FLS980 spectrometer.

Transmission electron microscope (TEM) measurement was performed on a JEM-100 CXII microscope, operating at an accelerating voltage of 80-120 kV. For the observation of dye aggregates, a drop of aggregate suspension (concentration: 0.5 mg/mL) was dropped on a 300 mesh Formvar copper grid coated with carbon. About 2 min after the deposition, the grid was tapped with filter paper to remove surface water and air-dried. Negative staining was performed by addition of a drop of aqueous solution of uranyl acetate (2 wt %). For dye **2**, very thin helical aggregates were observed, and their TEM images are not sufficiently clear, because that negative staining do not work for so thin aggregates with the diameter less than 2 nm.

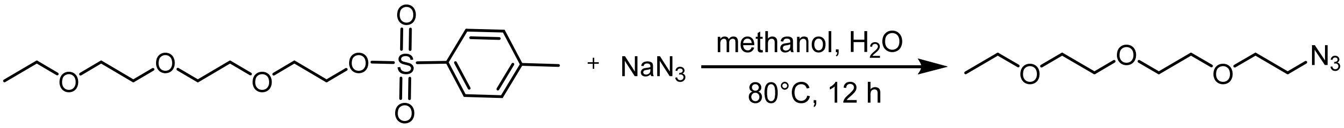
Atomic force microscope (AFM, Dimension 3000, Digital instrument) measurement was performed in the tapping mode under ambient conditions. A drop of aggregate suspension (concentration: 0.5 mg/mL) was dropped on the mica surface. AFM measurement was performed after the surface water was volatilized naturally at room temperature.

Preparation of aggregates: Dye **1** or **2** (1.0 mg) was dissolved in tetrahydrofuran (1.0 mL, THF), and deionized water (9.0 mL) was then slowly added into the THF solution. These aggregates were then further purified by dialysis against deionized water using a dialysis membrane (MWCO 12000) to remove THF and small molecular monomers.

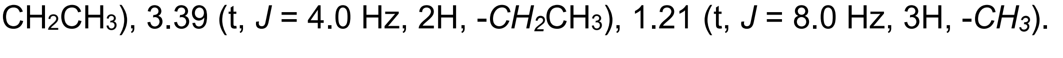
2. Synthesis and characterizations



In a 100 mL round bottom flask, triethylene glycol ether (5 mL, 28.6 mmol) was dissolved in triethylamine (20 mL, 144 mmol), the reaction system was cooled to 0 °C, *p*-toluenesulfonyl chloride (6 g, 31.4 mmol) was slowly added, and the reaction mixture was slowly raised to room temperature, and reacted for 5 h at room temperature. After the reaction was completed, the reaction mixture was slowly added dropwise to the stirred mixture of concentrated hydrochloric acid and crushed ice, and then extracted for three times with ether. The organic phases were combined, and washed with saturated sodium bicarbonate solution, dried over anhydrous $MgSO_4$, then filtered to give a colorless transparent oil (8.1 g, 24.3 mmol) with a yield of 85.1%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 2H, -*ArH*), 7.35 (d, *J* = 8.0 Hz, 2H, -*ArH*), 4.16 (t, *J* = 4.0 Hz, 2H, -CH_2OSO_2Ar), 3.69 (t, *J* = 8.0 Hz, 2H, -$CH_2CH_2OSO_2Ar$), 3.62–3.55 (m, 8H, -$OCH_2CH_2OCH_2CH_2O$-), 3.52 (dd, *J* = 4.0 Hz, 8.0 Hz, 2H,), 2.45 (s, 3H, -$ArCH_3$), 1.20 (t, *J* = 8.0 Hz, 3H, -CH_2CH_3).

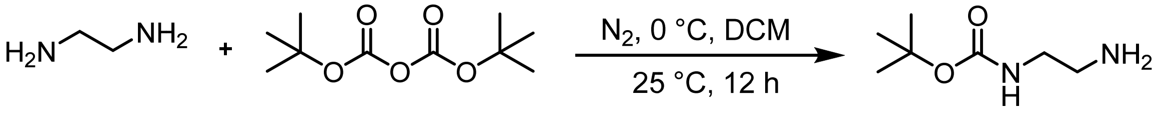


1-Azido-2- (2- (2-ethoxyethoxy) ethoxy) ethane: In a 100 mL round bottom flask, 4-methylbenzenesulfonic acid 2 -(2- (2-ethoxyethoxy) ethoxy) ethyl ester (1.66 g, 5 mmol) and sodium azide (0.65 g, 10 mmol) were added into H_2O/methanol (1/3, v/v, 10 mL). The reaction mixture was stirred and refluxed at 80 °C for 12 h. After the reaction was completed, NaOH (0.24 g) was added to remove unreacted NaN_3, the reaction mixture was washed with water, extracted with dichloromethane, the organic phase was collected, dried over anhydrous sodium sulfate, filtered under reduced pressure, and the crude product was obtained by rotary evaporation. The crude product was then purified by column chromatography (eluent: petroleum ether / ethyl acetate = 3 / 1, v / v) to give colorless oil (0.61 g, 3.0 mmol) with a yield of 60.1%. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69–3.64 (m, 8H, N_3-$CH_2CH_2OCH_2CH_2$-), 3.61–3.58 (m, 2H, N_3-$CH_2CH_2OCH_2CH_2OCH_2$-), 3.53 (dd, *J* = 4.0 Hz, 8.0 Hz, 2H, -$CH_2OCH_2CH_3$), 3.39 (t, *J* = 4.0 Hz, 2H, -CH_2CH_3), 1.21 (t, *J* = 8.0 Hz, 3H, -CH_3).

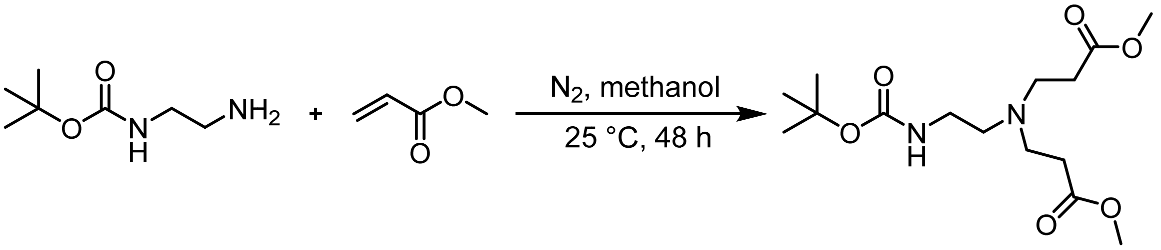


2- (2- (2-Ethoxyethoxy) ethoxy) ethane-1-amine: The anhydrous tetrahydrofuran solution (2 mL) of triphenylphosphine (0.82 g, 3.13 mmol) was added dropwise to the anhydrous tetrahydrofuran solution (2 mL) of 1-azido-2- (2- (2-ethoxyethoxy) ethoxy) ethane (0.20 g, 2.50 mmol). The reaction mixture was stirred at room temperature for 5 h, and distilled water

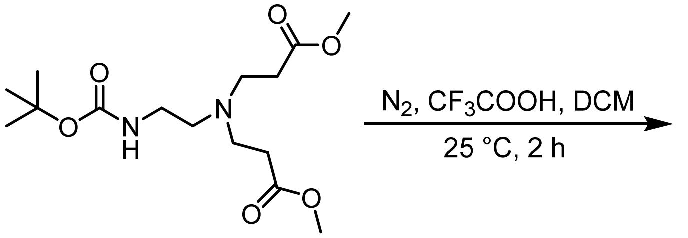
(2 mL) was then added. The reaction mixture was refluxed at 80 °C for 12 h. The crude product was obtained by rotary evaporation, which was purified by column chromatography (eluent: dichloromethane/methanol = 9 /1, v / v) to give light yellow oil (0.44 g, 2.48 mmol) with a yield of 99.1%.^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69–3.63 (m, 8H, H_2N-$\mathit{CH_2CH_2OCH_2CH_2}$-), 3.61–3.59 (m, 2H, H_2N-$CH_2CH_2OCH_2CH_2O$$\mathit{CH_2}$-), 3.54 (dd, J = 4.0 Hz, 8.0 Hz, 2H, -$\mathit{CH_2}$$OCH_2CH_3$), 3.40 (t, J = 4.0 Hz, 2H, -$\mathit{CH_2}$$CH_3$), 2.18 (s, 2H, -$\mathit{NH_2}$), 1.22 (t, J = 4.0 Hz, 3H, -$\mathit{CH_3}$).



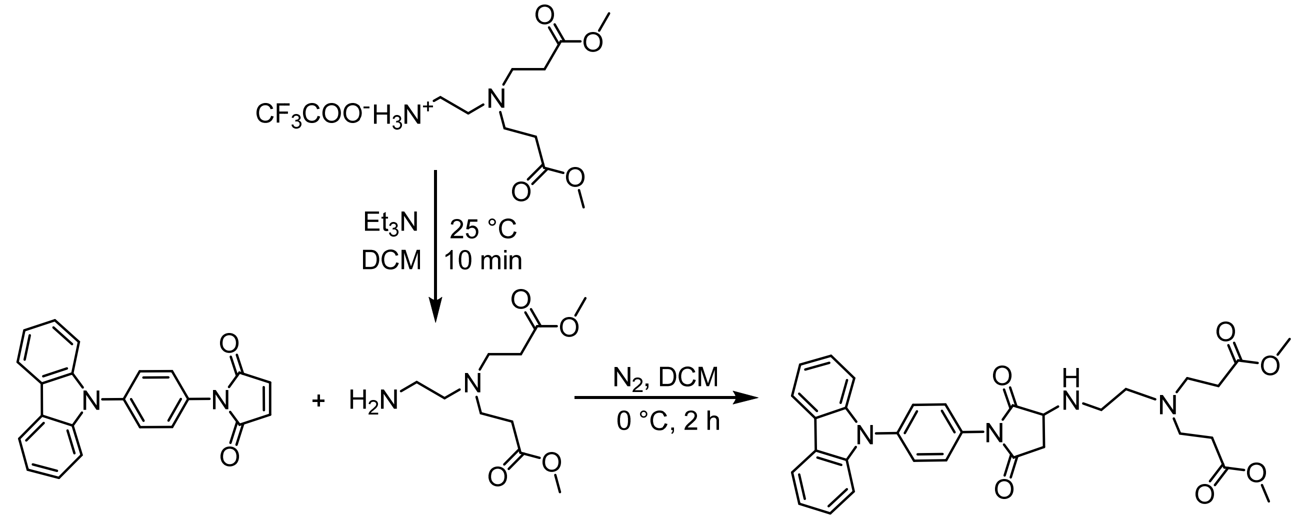
In an ice water bath, ethylenediamine (4.81 g, 80.00 mmol) and dichloromethane (40 mL) were add to a three-necked flask in N_2 atmosphere. A dichloromethane solution (10 mL) of di-tert-butyl dicarbonate (2.18 g, 10.00 mmol) was slowly added dropwise to the reaction flask. The reaction mixture was kept at room temperature for 12 h. The reaction solvent dichloromethane was removed under reduced pressure, and deionized water (50 mL) was then added with stirring, and the product mixture was then filtered. NaCl (1.0 g) was added to make it a saturated solution and extracted with ethyl acetate. Organic phase was collected and concentrated. The crude product was purified by column chromatography (eluent: methanol) to give colorless oil (10.42 g, 6.51 mmol) with a yield of 65.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (s, 1H, -CONH-), 3.20–3.16 (q, 2H, -HN-$\mathit{CH_2}$-), 2.80 (t, J = 4.0 Hz, 2H, -$\mathit{CH_2}$$NH_2$), 1.88 (s, 2H, -$\mathit{NH_2}$), 1.45 (t, J = 4.0 Hz, 9H, 3x-$\mathit{CH_3}$).



Under ice water bath, the methanol solution (15 mL) methyl acrylate (2.58 g, 30.00 mmol) was dropwise added to the methanol solution (20 mL) of (2-aminoethyl) carbamate (1.60 g, 10.00 mmol) in N_2 atmosphere. The reaction mixture was stirred at room temperature for 48 h, and then concentrated. Crude product was purified by column chromatography (eluent: methanol / dichloromethane = 1 / 20, v / v) to give colorless oil (1.66 g, 5.01 mmol) with a yield of 50.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.13 (s, 1H, -CONH-), 3.70 (s, 6H, -COO$\mathit{CH_3}$), 3.20–3.15 (q, 2H, -HN-$\mathit{CH_2}$-), 2.78–2.73 (m, 4H, 2-N$\mathit{CH_2}$-), 2.53 (t, 2H, J = 8.0 Hz, -$NCH_2$$\mathit{CH_2}$-$NR_2$), 2.45–2.41(m, 4H, 2-$\mathit{CH_2}$$COOCH_3$), 1.45 (s, 9H, -O($\mathit{CH_3}$)$_3$).



Under ice water bath, the dichloromethane (3 mL) solution of trifluoroacetic acid (3 mL) was dropwise added to the dichloromethane (5 mL) of 3, 3'-((2-((tert-butoxycarbonyl) amino) ethyl) azadiyl) dimethyl propionate (3.32 g, 10.00 mmol) in N_2 atmosphere. The reaction mixture was kept at room temperature for 2 h, and then concentrated by rotary evaporation. Crude product was preliminarily purified by dissolving in methanol and precipitating in diethyl ether and n-hexane for three times. Crude product was then dried in vacuum and further purified by column chromatography (eluent: methanol /dichloromethane = 1 / 10, v / v) to give colorless oil (1.23 g, 35.5 mmol) with a yield of 35.5%.



Dye **1**. Under a nitrogen atmosphere, 0.42 g (1.2 mmol) of 2-(bis(3-methoxy-3-oxypropyl)amino)-1-amine1,2,2,2-trifluoroacetate, 0.4 mL triethylamine and 2 mL dichloromethane were added to a 100 mL three-necked round-bottom flask, and stirred at room temperature for 10 min. 0.38 g (1.0 mmol) of *N*-phenylcarbazolyl maleimide was dissolved in 4 mL of dichloromethane, and slowly added dropwise to the above round bottom flask at 0 °C and reacted for 1 h. Crude product was purified by column chromatography (eluent: ethyl acetate) to give compound **1** (0.25 g, 0.44 mmol) as a pale yellow viscous substance with a yield of 43.9%.

^{1}H NMR (400 MHz, $CDCl_3$, Figure S1): δ = 8.14 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.69 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.58 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.48-7.42 (m, 4H, Ar*H*), 7.30 (t, *J* = 8.0 Hz, 2H, Ar*H*), 4.00 (dd, *J* = 4.0, 8.0 Hz, 1H, -CO-C*H*(R)-), 3.70 (s, 6H, 2x-O-CH_3), 3.22-3.15 (q, 1H, -N*H*-), 3.03–2.97 (m, 2H, -CO-CH_2-), 2.88–2.60 (m, 8H, 2x-NH-CH_2CH_2-), 2.55–2.42 (m, 4H, 2x-CH_2-$COOCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$, Figure S2): δ = 176.70, 174.51, 173.10, 140.61, 137.78, 130.56, 127.89, 127.49, 126.09, 123.54, 120.34, 120.25, 109.81, 56.39, 53.44, 51.71, 49.12, 45.10, 36.53, 32.50.

MS: m/z calculated for $C_{32}H_{34}N_4O_6[M+Na]^+$: 593.2, found: 593.3.

IR (cm^{-1}): 3451, 3047($\nu_{N\text{-}H}$), 2945(ν_{CH_3}), 2916(ν_{CH_2}), 2843(ν_{CH_2}), 1711($\nu_{C=O}$), 1642, 1512, 1449, 1359, 1228, 1174, 831, 749, 721.

Fluorescence (dichloromethane, λ_{ex}= 295 nm)(λ_{em}= 342 nm, 365 nm; fluorescence quantum yield: Φf = 0.42; fluorescence lifetime (τ= 5.7 ns in THF, 4.8 ns in dichloromethane).

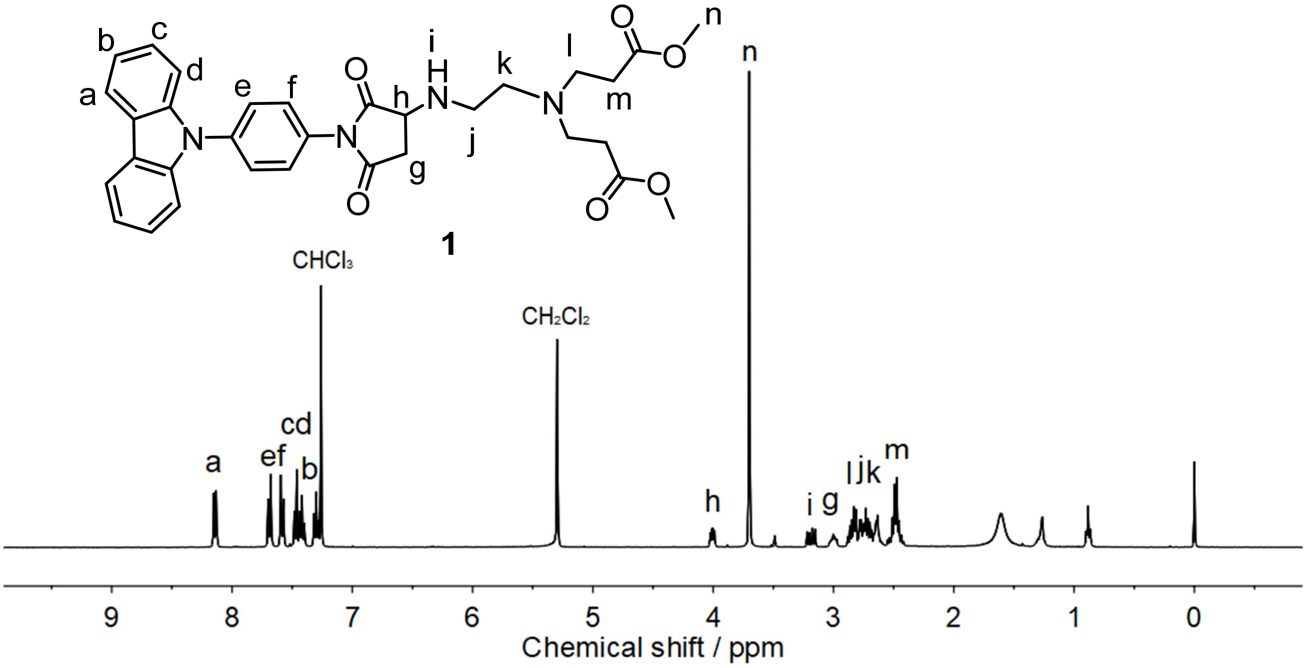


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ and its chemical structure with corresponding signal assignments.

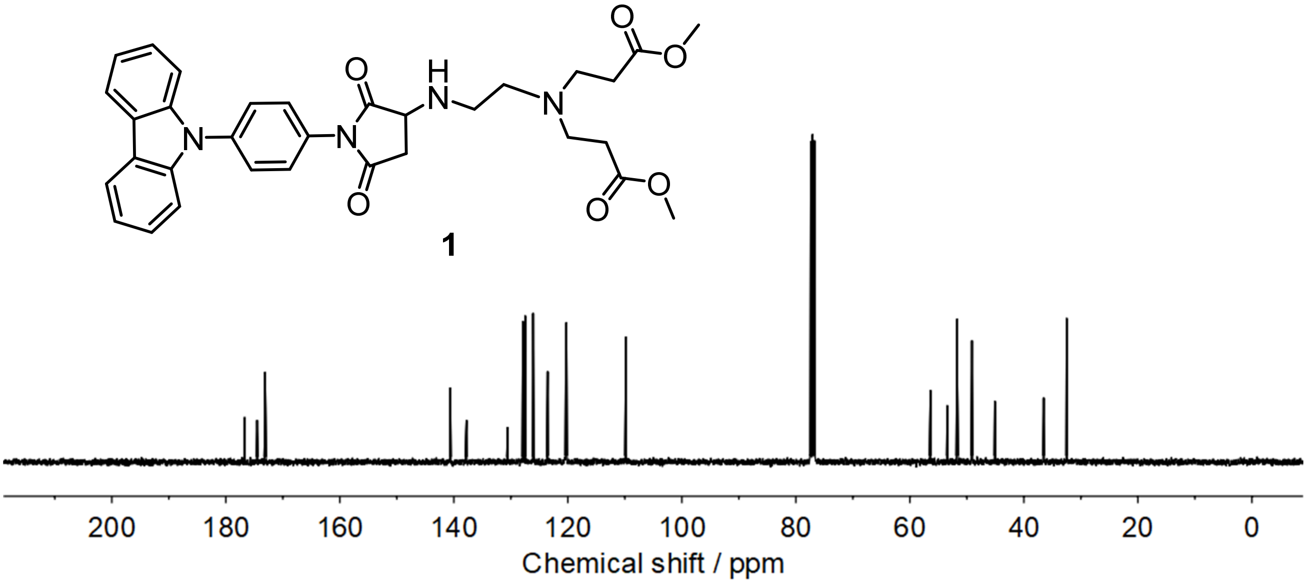
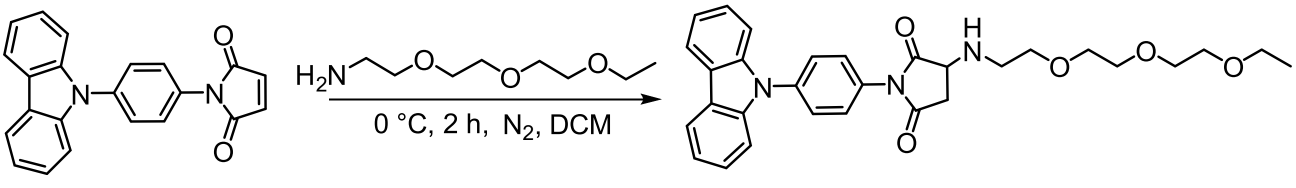


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.



2

Dye **2**: A dichloromethane solution (5 mL) of *N*-phenylcarbazolyl maleimide (0.34 g, 1.00 mmol) was slowly added to the dichloromethane solution (2 mL) of 2-(2-(2-ethoxyethoxy) ethoxy) ethane-1-amine (0.27 g, 1.50 mmol) at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 2 h, and then concentrated under reduced pressure. Crude product was purified by silica gel column chromatography (eluent: ethyl acetate / dichloromethane = 2 / 1, v / v) to give **2** (0.28 g, 0.5 mmol) as white oil with a yield of 54.4%.

^{1}H NMR (400 MHz, $CDCl_3$, Figure S3): δ = 8.14 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.69 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.56 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.49-7.42 (m, 4H, Ar*H*), 7.30 (t, *J* = 8.0 Hz, 2H, Ar*H*), 4.05–4.01 (m, 1H, -CO-C*H*(R)-), 3.68-3.51 (m, 10H, -CH_2-O-CH_2CH_2-O-CH_2CH_2-), 3.22-3.15 (q, 1H, -N*H*-), 3.09–3.04 (m, 2H, -CO-CH_2C*H*(R)-), 2.83–2.77 (m, 2H, -NH-CH_2-). 1.22 (t, 3H, -OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, Figure S4): δ = 173.96, 171.23, 140.51, 138.24, 130.02 128.16, 127.57, 126.12, 123.55, 120.36, 120.31, 109.81, 60.44, 52.04, 48.26, 44.44, 31.62, 29.73, 22.63, 21.09, 14.22, 14.16.

HRMS (ESI): m/z calculated for $C_{30}H_{33}N_3O_5$ [M+H]$^+$: 516.2498, found: 514.2495.

IR (cm^{-1}): 3438, 3062($\nu_{N\text{-}H}$), 2953(ν_{CH3}), 2924(ν_{CH2}), 2867(ν_{CH2}), 1724($\nu_{C=O}$), 1595, 1576, 1513, 1460, 1450, 1380, 1280, 1119, 1071, 1035, 958, 938, 786, 743, 703.

Fluorescence (dichloromethane, λ_{ex}= 295 nm): λem= 342 nm, 365 nm; fluorescence quantum yield: Φf = 0.40; fluorescence lifetime (τ= 5.8 ns in THF, 4.7 ns in dichloromethane).

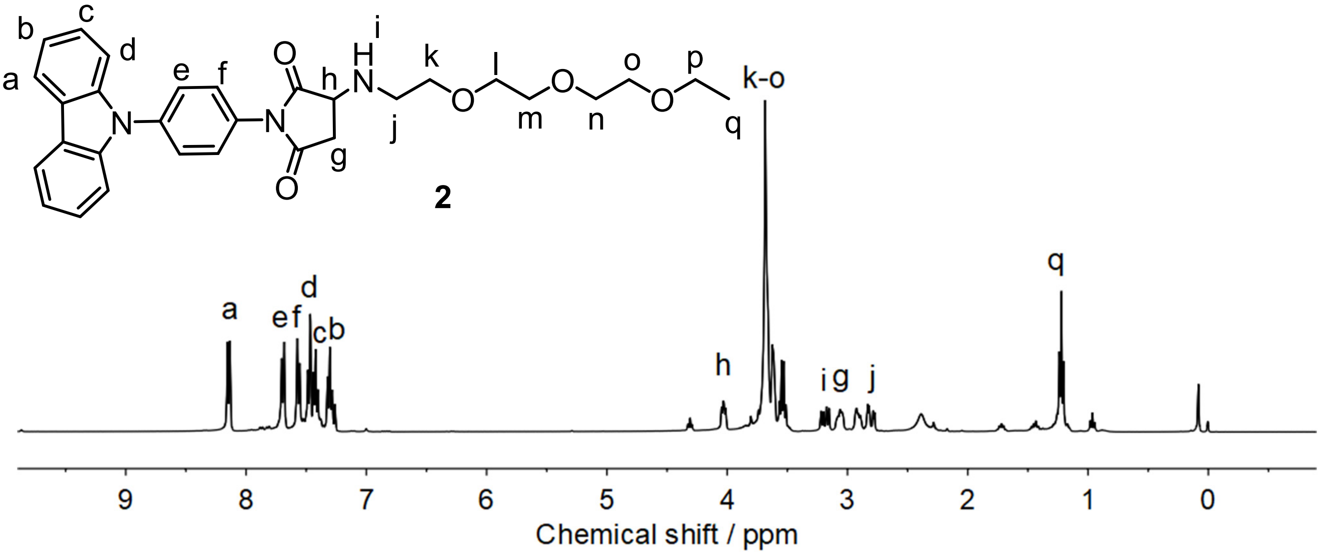


Figure S3. ^{1}H NMR spectrum of dye **2** in $CDCl_3$ and its chemical structures with corresponding signal assignments.

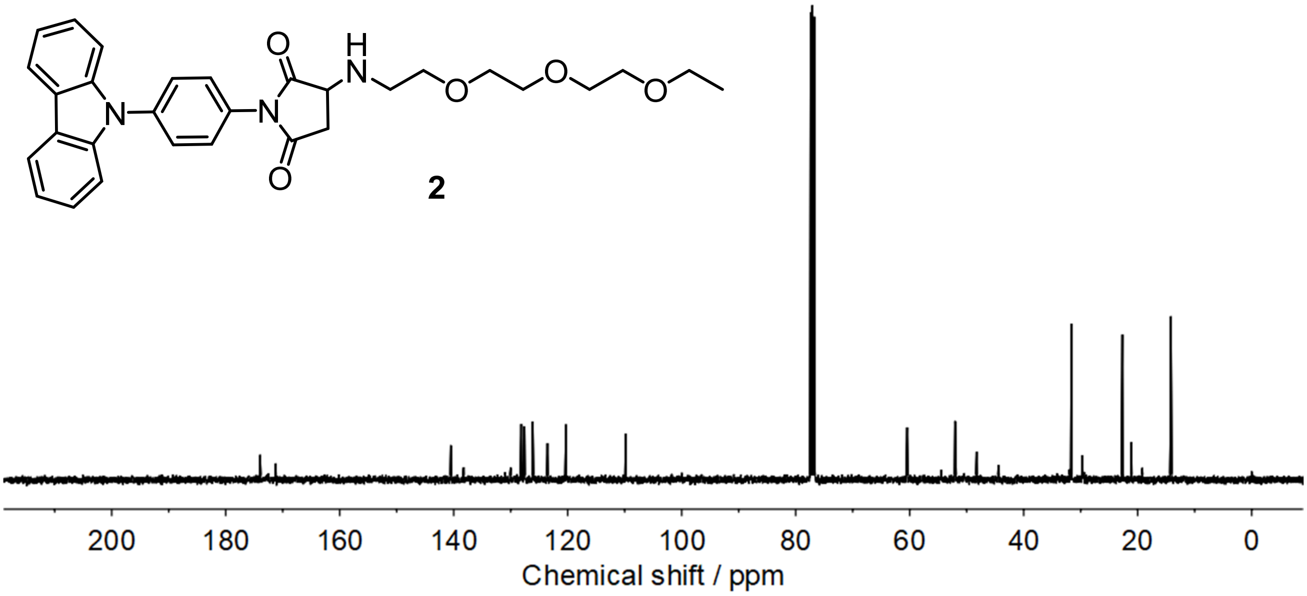
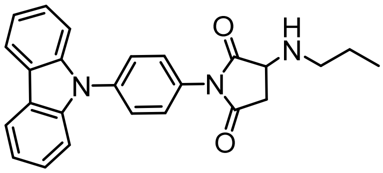


Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$.



M

Model compound **M**. A dichloromethane solution (5 mL) of *N*-phenylcarbazolyl maleimide (0.34 g, 1.00 mmol) was slowly added to the dichloromethane solution (2 mL) of *n*-propylamine (0.09 g, 1.50 mmol) at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 2 h, and then concentrated under reduced pressure. Crude product was purified by silica gel column chromatography (eluent: ethyl acetate / dichloromethane = 1 / 20, v / v) to give model compound (0.22 g, 0.55 mmol) as white oil with a yield of 55.4%.

^{1}H NMR (400 MHz, $CDCl_3$, Figure S5): δ = 8.16 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.70 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.57 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.50–7.41 (m, 4H, Ar*H*), 7.32 (t, *J* = 4.0 Hz, 2H, Ar*H*), 3.99–3.96 (m, 1H, -CO-C*H*(R)-), 3.18–3.11 (q, 1H, -N*H*-), 2.81–2.64 (m, 4H, $\text{-CO-C}H_2\text{-}$, $\text{-C}H_2\text{CH}_2\text{C}H_3$), 1.65–1.56 (m, 2H, $\text{-C}H_2\text{C}H_3\text{-}$), 1.01 (t, 3H, $\text{-CH}_2\text{C}H_3$).

^{13}C NMR (100 MHz, $CDCl_3$, Figure S6): δ = 176.97, 174.28, 140.59, 137.91, 130.34, 127.80, 127.56, 126.15, 123.57, 120.39, 120.33, 109.82, 56.53, 49.68, 36.52, 23.26, 11.75.

HRMS (ESI): m/z calculated for $C_{25}H_{23}N_3O_2$ $[M\text{-}H]^-$: 396.1707, found: 396.1707.

IR (KBr pellet, cm^{-1}): 3456, 3047($\nu_{N\text{-}H}$), 2949(ν_{CH3}), 2924(ν_{CH2}), 2866(ν_{CH2}), 1709($\nu_{C=O}$), 1599, 1515, 1448, 1395, 1357, 1223, 1188, 737, 719, 919, 828.

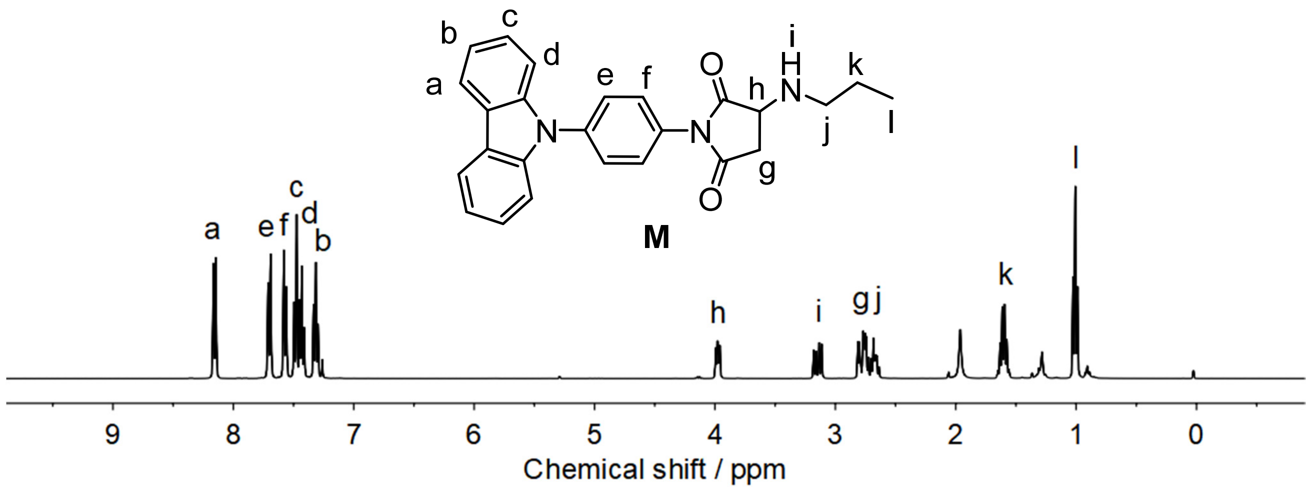


Figure S5. ^{1}H NMR spectrum of model compound in $CDCl_3$ and its chemical structures with corresponding signal assignments.

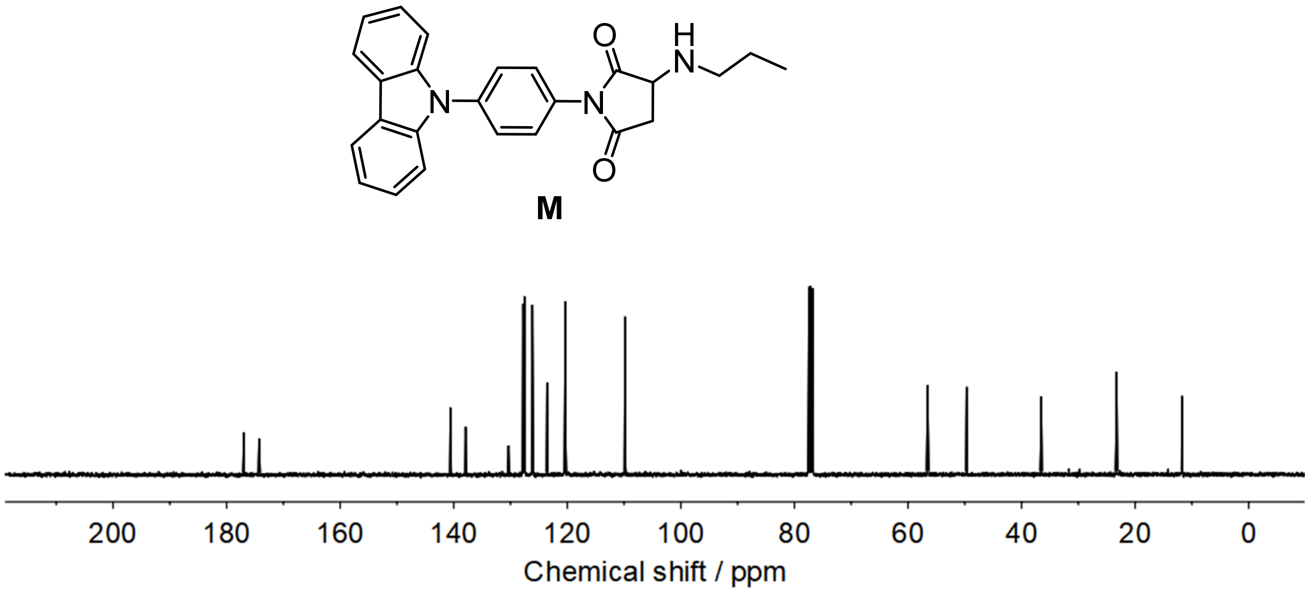


Figure S6. ^{13}C NMR spectrum of model compound in $CDCl_3$.

3. Single-crystal X-ray diffraction

Table S1. Crystal data and structure refinement for model compound **M**.

Identification code	**M**
Empirical formula	$C_{25}H_{23}N_3O_2$
Formula weight	398.47
Temperature	273 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 4.3990(8) Å α = 71.730(4)°
	b = 13.512(2) Å β = 90°
	c = 18.260(3) Å γ = 80.6300°
Volume	1015.4(3) Å^3
Z, Calculated density	2, 1.300 Mg/m^3
Crystal shape/ Crystal color	block/colorless
Absorption coefficient	0.084 mm^{-1}
F (000)	422
Crystal size	0.19 × 0.15 × 0.13 mm^3
Theta range for data collection	2.28 to 27.21°
Limiting indices	$-5 \le h \le 5$, $-17 \le k \le 17$, $-23 \le l \le 23$
Reflections collected / unique	13347/7055 [R(int) = 0.0466]
Completeness to	71.1 %
Theta (max)	27.802
Absorption correction	Semi-empirical from equivalents
Data / restraints / parameters	3428 / 0 / 275
Goodness-of-fit on F^2	0.946
Final R indices [I>2sigma(I)]	R_1 = 0.0648, wR_2 = 0.1983
R indices (all data)	R_1 = 0.1058, wR_2 = 0.2313
Largest diff. peak and hole	0.234 and -0.249 e. Å^{-3}

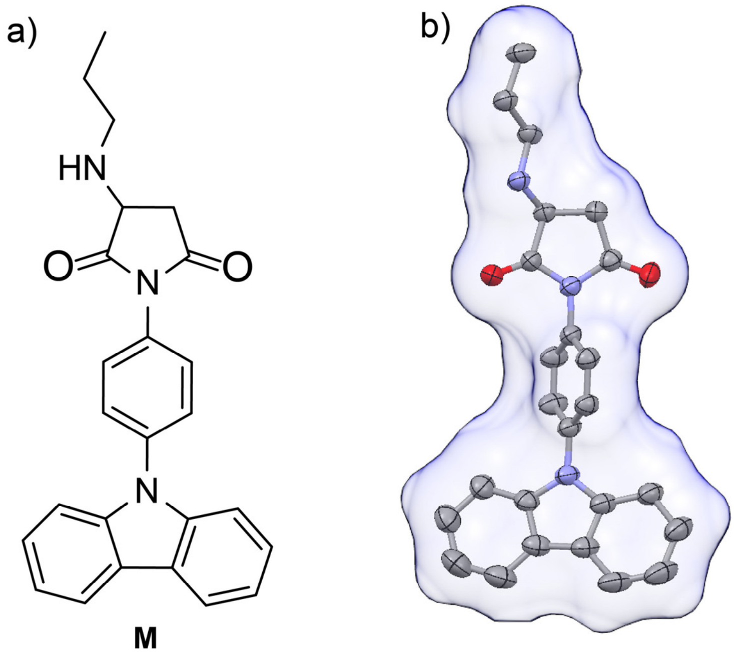


Figure S7. (a) Chemical structure of model compound **M**. (b) Molecular structures (Oak Ridge Thermal Ellipsoid Plot, ORTEP) of model compound **M** determined by single-crystal X-ray diffraction, top view (left) and side view (right). Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms are omitted for clarity.

4. UV-vis absorption and fluorescence spectroscopy

Fluorescence spectroscopy. Steady-state fluorescence spectra in solution were recorded on an Edinburgh Instruments FLS980. Fluorescence decay was analyzed using a least squares interaction convolution method. The fluorescence quantum yields of **1** and **2** were calculated using the following equation:

$$\Phi = \Phi_r \frac{I}{A} \frac{A_r}{I_r} \frac{\eta^2}{{\eta_r}^2}$$

where *I* is the integrated area under the emission band of the dye sample solution; *A* is the optical density of the sample solution at the excitation wavelength and η is the refractive index of the solvent. The optical density of the sample solution used to calculate the fluorescence quantum yields was less than 0.1 at the excitation wavelength. The reference was selected from a cyclohexane solution of 9,10-diphenylanthracene (Φ_r = 0.90).[1-2] Fluorescence lifetimes were recorded on an Edinburgh Instruments FLS980 equipping with a nanosecond flash lamp as the excitation light source. The instrument response function was collected by scattering the excitation light of a 30% silica suspension aqueous solution.

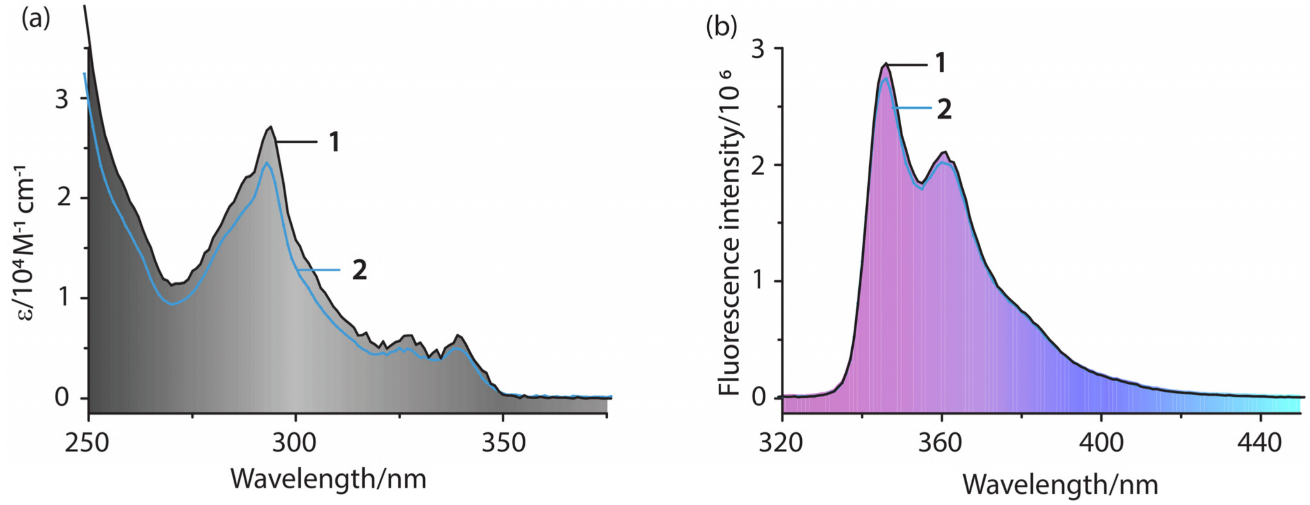


Figure S8. UV/vis absorption (a) and fluorescence emission spectra (b) of dyes **1** and **2** in dichloromethane (DCM), λ_{ex} = 295 nm, λ_{em} = 342 nm, [**1**] = [**2**] = 2.0×10^{-5} M.

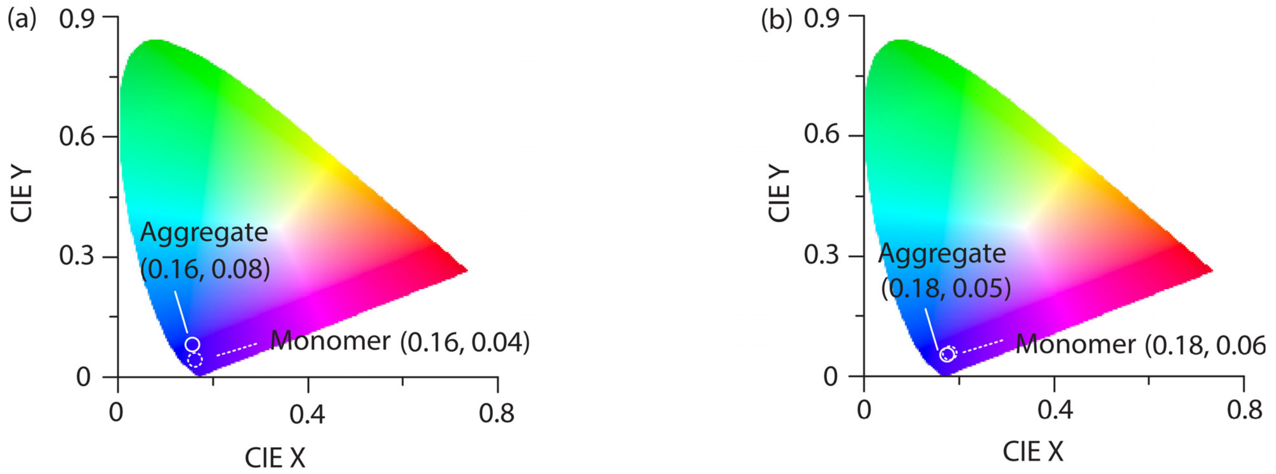


Figure S9. CIE 1931 chromaticity diagram. The circle points are fluorescence colour coordinates of monomers (0.16, 0.04) and aggregates (0.16, 0.08) of **1** (a), and monomers (0.18, 0.06) and aggregates (0.18, 0.05) of **2** (b)**.** Solvents of monomers and aggregates are tetrahydrofuran (THF) and aqueous solution (H_2O/THF=9/1), respectively. [**1**] = [**2**] =4×10^{-5} M.

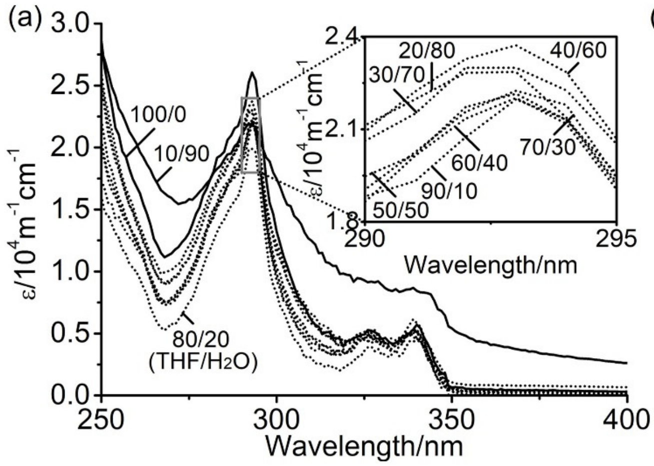


Figure S10. UV-vis absorption spectra of **1** (a) and **2** (b) at the concentration of 4×10^{-5} M in different THF/H$_2$O ratios, λ_{ex} = 295 nm.

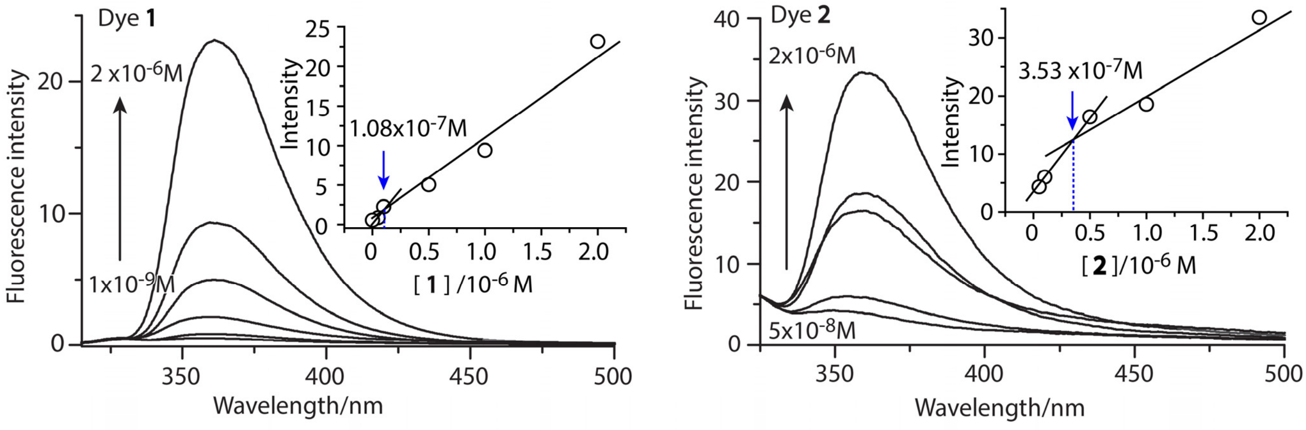


Figure S11. Fluorescence spectral changes of **1**(Left) and **2**(Right) with increasing concentration in aqueous solution (H$_2$O/THF=9/1), λ_{ex} = 295 nm. Insets: Plots of fluorescence intensity versus concentration, 1.08×10^{-7} M and 3.53×10^{-7} M are critical aggregation concentration of **1** and **2**, respectively.

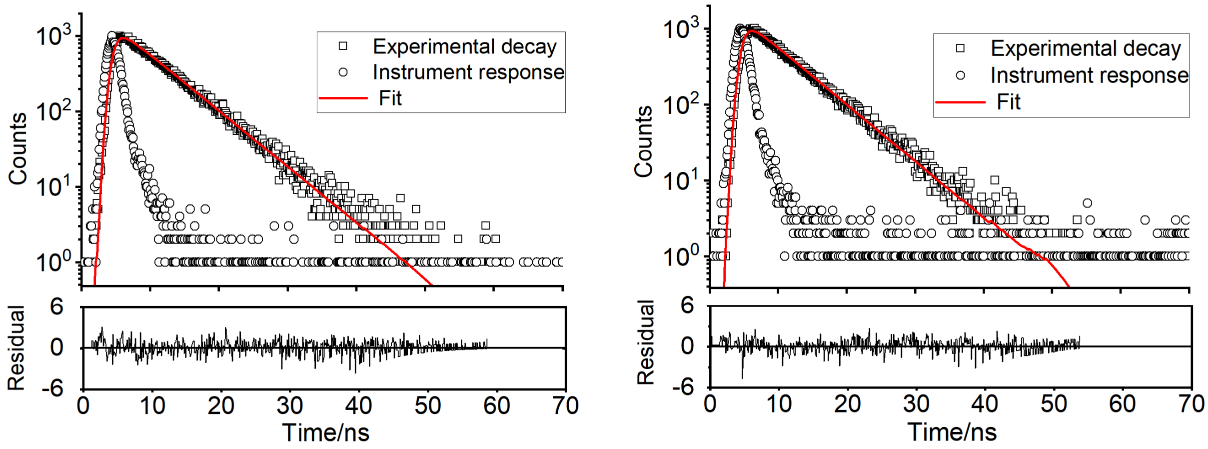


Figure S12. Fluorescence decays of monomers of dyes **1** (Left) and **2** (Right) in THF. λ_{ex} = 295 nm, λ_{em} = 360 nm, *c*= 1×10^{-5} M. Fluorescence decays of **1** and **2** indicate single-exponential decays and the fluorescence lifetimes are fitted to be 5.7 ns (χ^2 = 1.02) for **1** and 5.8 ns (χ^2 = 0.93) for **2**, respectively.

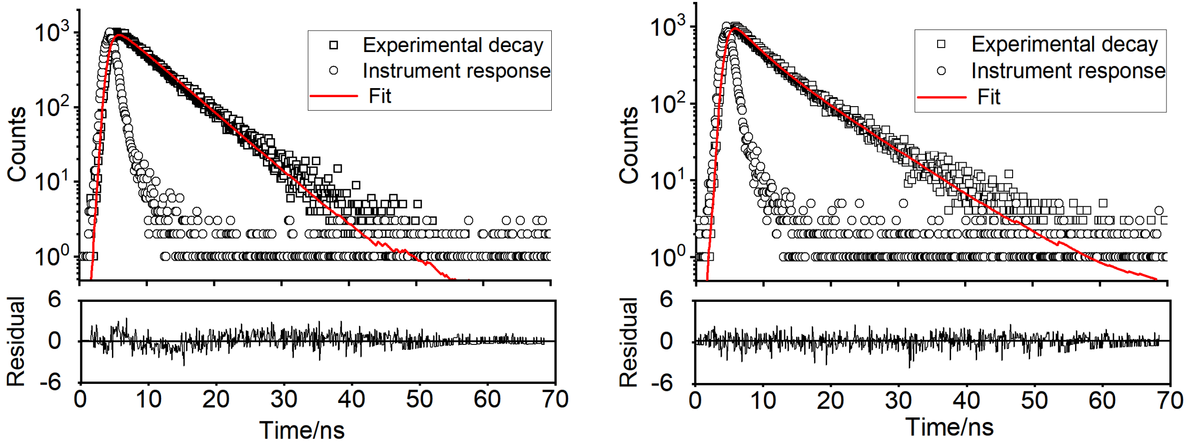


Figure S13. Fluorescence decays of aggregates of dyes **1** (Left) and **2** (Right) in aqueous solution (H_2O/THF=9/1). λ_{ex} = 295 nm, λ_{em} = 360 nm, *c*= 1×10^{-5} M. Average fluorescence lifetimes are fitted to be $<\tau>$= 6.1 ns (τ_1 = 2.7 ns, 28%; τ_2 = 7.5 ns, 72%; χ^2 = 0.94) for **1**, and 5.6 ns (χ^2 = 1.01) for **2**, respectively.

5. Transmission electron microscope and atomic force microscopy

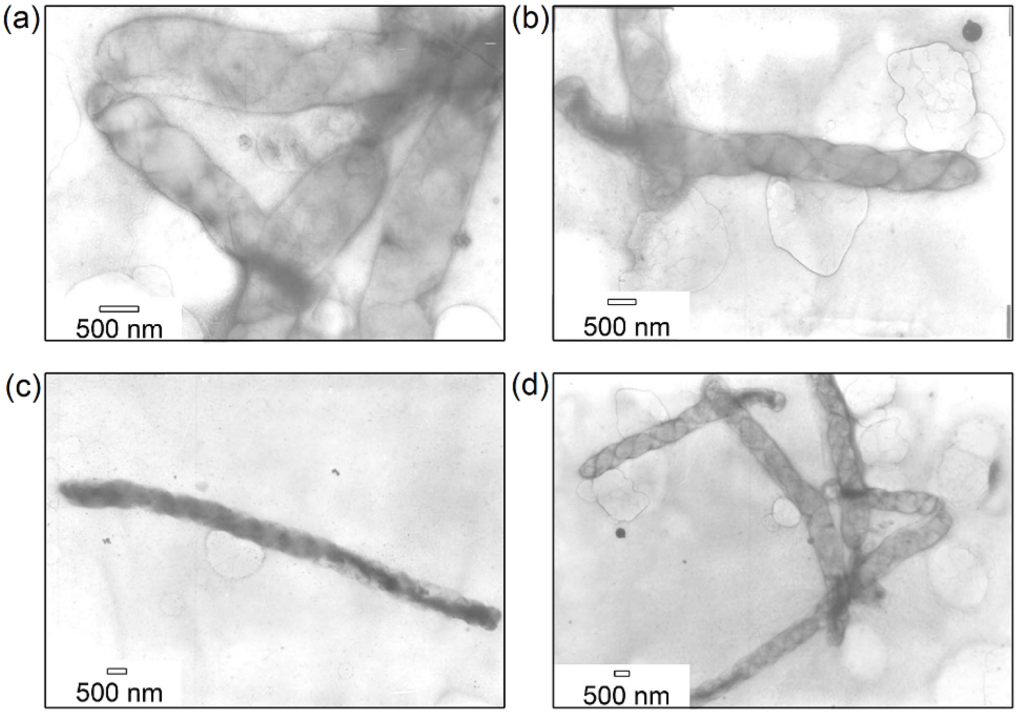


Figure S14. TEM images of aggregates of dye **1** prepared from deionized water, [**1**] = 1.7×10^{-4} M.

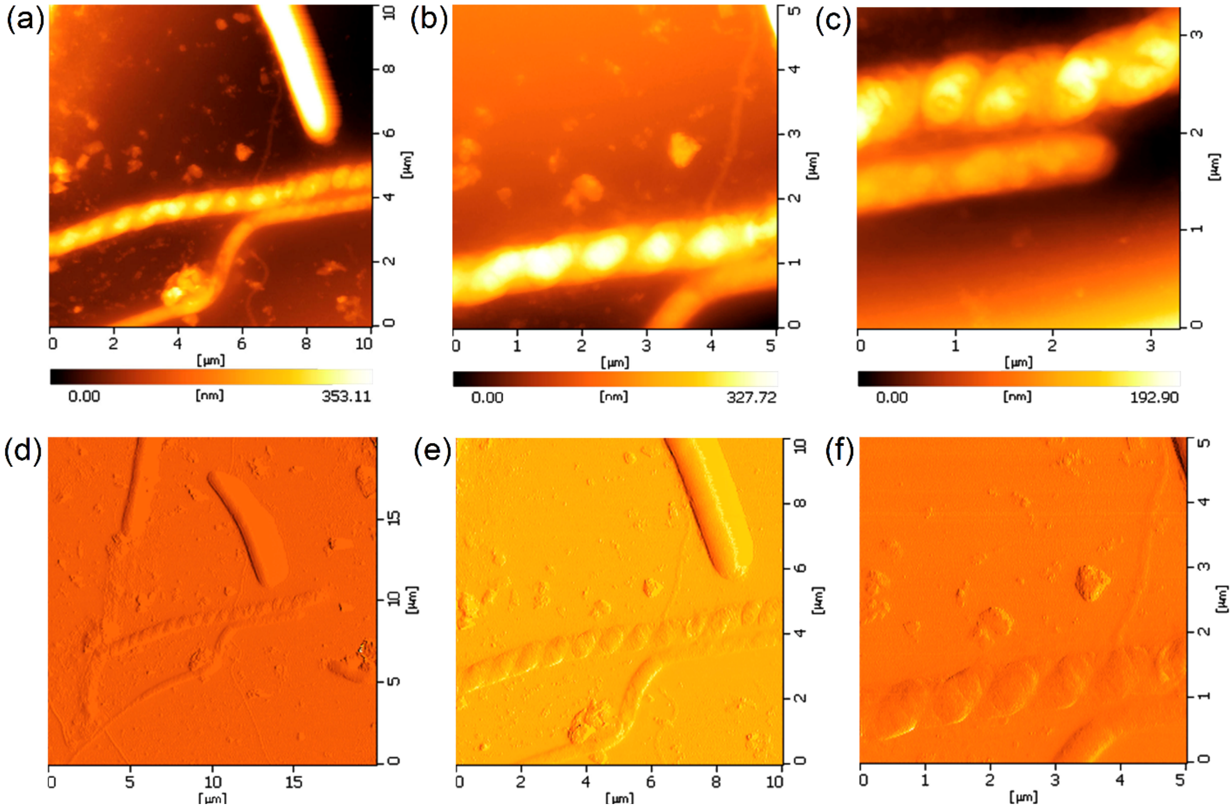


Figure S15. AFM images ((hight (a, b, c) and phase (d, e, f)) of aggregates of dye **1** prepared from deionized water, [**1**] = 1.7×10^{-4} M.

6. References

[1] D. Eaton, *Pure Appl. Chem.*, 1988, **60**, 1107.

[2] F. Li, X. Li, Y. Wang and X. Zhang, *Angew. Chem. Int. Ed.*, 2019, **58**, 17994.