Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary information

Dynamic Diels-Alder reactions of maleimide-furan amphiphiles and their fluorescence ON/OFF behaviours

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1. Materials and Methods

All chemicals were purchased and used without further purification. IR spectra were recorded on a Bruker ALPHA II FTIR spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker miorOTOF-QII with ESI. UV/Vis spectra were measured with Agilent Varian Cary 300 spectrometer. Fluorescence quantum yields (*Φ*) were calculated according to the equation as follows:

$$\phi = \phi_{\mathrm{r}} \frac{I}{I_{\mathrm{r}}} \frac{OD_{\mathrm{r}}}{OD} \frac{n^2}{n_{\mathrm{r}}^2}$$

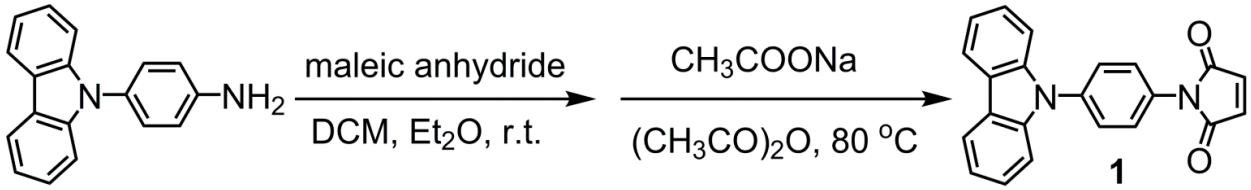
where A and A_r are the sample and reference absorbance at the excitation wavelength, respectively, I is the area under the corrected emission spectrum, and n is the refractive index of the used solvents. The 9, 10-diphenylanthrene in cyclohexane (ϕ_r = 0.90) was used as a reference.[1] X-ray crystal data of **2** were collected at an Agilent Technologies SuperNova Single Crystal Diffractometer equipped with graphite monochromatic Mo *Kα* radiation (λ = 0.71073 Å).

NMR spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilance (TMS) as an internal standard.

Fluorescence spectroscopy. The time-resolved fluorescence lifetimes were measured with an Edinburgh Instruments FLS980 following excitation by a nanosencond flash lamp. The steady-state fluorescence spectra were recorded with the slit width of both monochromators of 0.7 nm.

TEM characterization. TEM measurements were performed on a HITACHI 7700 electron microscopy operating at an acceleration voltage of 80-120 kV. A drop of sample solution was first placed on 300-mesh copper grid coated with carbon, and was left to stand for 2 minutes. Then, the grid was tapped with filter paper to remove water for twice. Negative staining was performed by addition of a drop of uranyl acetate aqueous solution (1%) to the sample copper grid. After 2 minutes, the surface water on the grid was removed by tapping with filter paper.

2. Synthesis and characterization



***N*-Phenylcarbazole maleimide 1** was synthesized according to the literature.[2] 4 mL of the dichloromethane solution of 4-(9*H*-carbazol-9-yl)benzenamine (0.387 g, 1.5 mmol) was added dropwise to the diethyl ether (5 mL) solution of maleic anhydride (0.22 g, 2.25 mmol) with stirring at room temperature for 2 h. The precipitate was collected by filtration. The mixture of the obtained maleamic acid (0.5 g), sodium acetate (0.21 g) and acetic anhydride (2.2 mL) was heated with stirring at 80 °C for 10 h. The precipitate was collect by suction filtration, and washed by water and ethanol successively for three times. The crude product was recrystallized in dichloromethane. Finally, yellow crystals (2.4 g, 47.3%) were obtained.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.7 Hz, 2H), 7.65 (dd, J = 29.2, 8.7 Hz, 4H), 7.46 (d, J = 8.1 Hz, 2H), 7.44 – 7.26 (m, 4H), 6.91 (s, 2H).

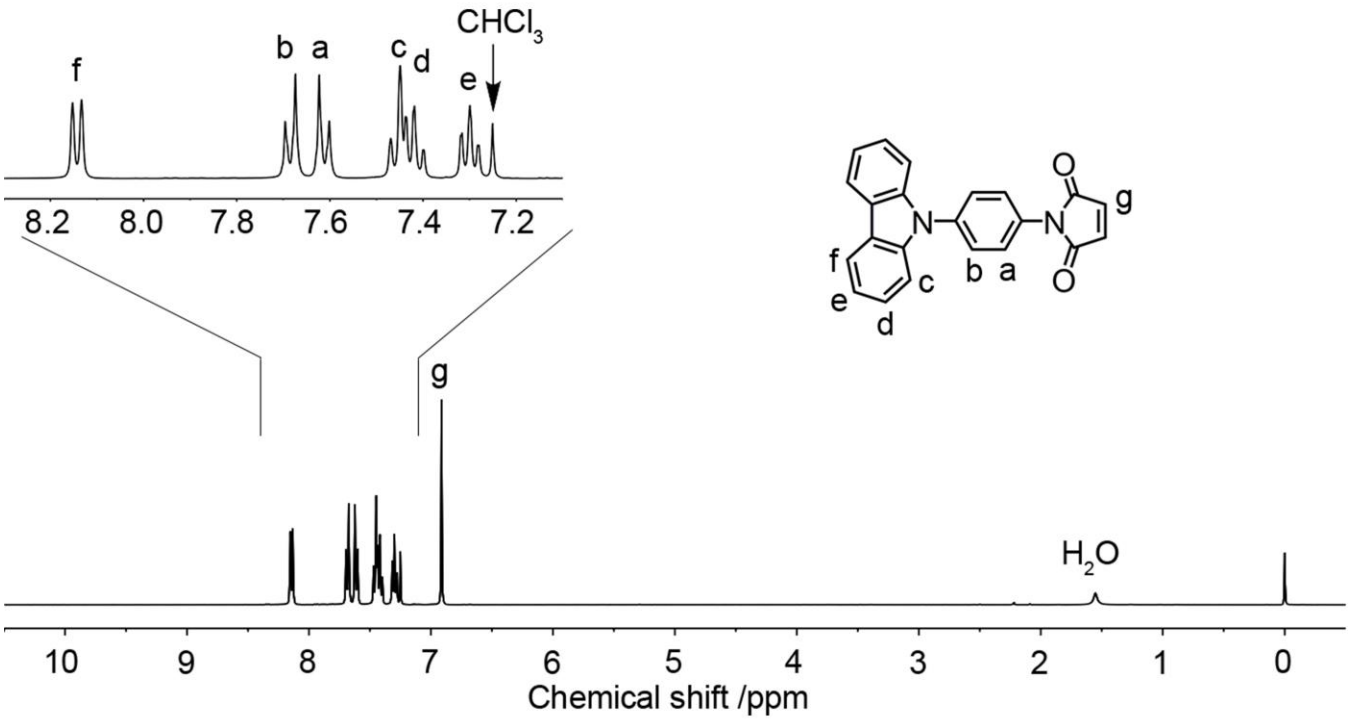
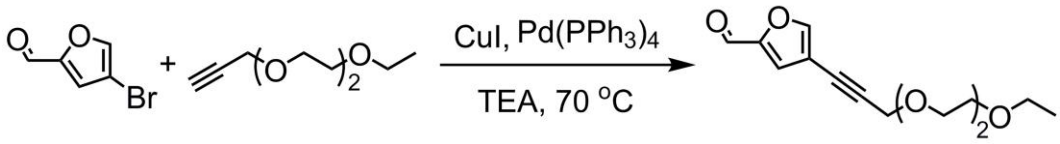


Fig. S1. ^{1}H NMR spectrum of *N*-phenylcarbazole maleimide **1** in $CDCl_3$ with corresponding assignments.



4-(3-{2-[2-(Ethoxy) ethoxy] ethoxy}-1-propynyl)-2-furancarbaldehyde was synthesized according to the literature with some modification.[3] 4-Bromo-2-furancarbaldehyde (0.35 g, 2 mmol) was dissolved in anhydrous triethylamine (10 mL) under N_2. Then, copper(I) iodide (0.0184g, 0.2 mmol) and tetrakis(triphenylphosphine)palladium (0) (0.2 g, 0.2 mmol) were added into the reaction solution. When the mixture was heated to 70 °C, 3-(2-(2-ethoxy) ethoxy) ethoxy)-1-propyne (0.41 g, 2.4 mmol) was added. After that, the mixture was further heated at 70 °C overnight with stirring. The solvent was evaporated under reduced pressure, and the mixture was extracted with petroleum ether (20 mL) for three times. The crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether = 1/4, *v*/*v*) to give a colorless oil (0.2 g, 33%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63 (s, 1H), 7.80 (s, 1H), 7.22 (d, *J* = 0.6 Hz, 1H), 4.39 (s, 2H), 3.76 – 3.49 (m, 10H), 1.20 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.66, 152.46, 150.28, 122.36, 110.10, 88.86, 75.31, 70.71, 70.42, 69.76, 69.39, 66.60, 58.98, 15.13.

HRMS (ESI): *m / z* calcd for $C_{14}H_{18}O_5$ $[M + Na]^+$: 289.1046; found: 289.1047.

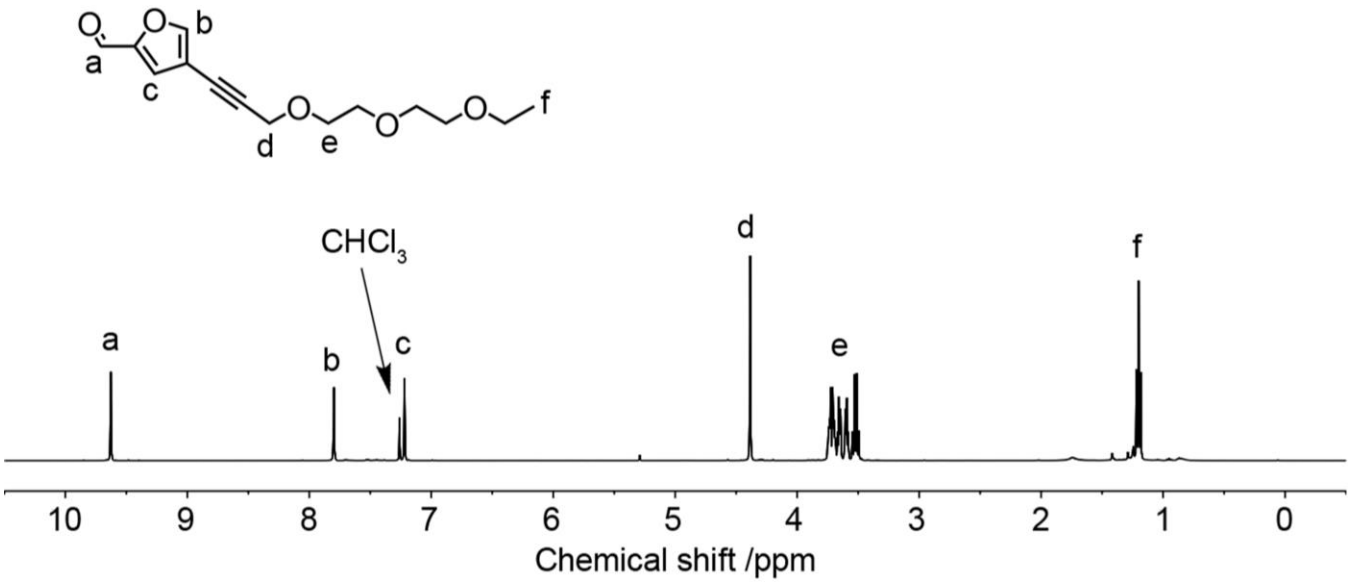


Fig. S2. ^{1}H NMR spectrum of 4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-1-propynyl)-2-furancarbaldehyde in $CDCl_3$ with corresponding assignments.

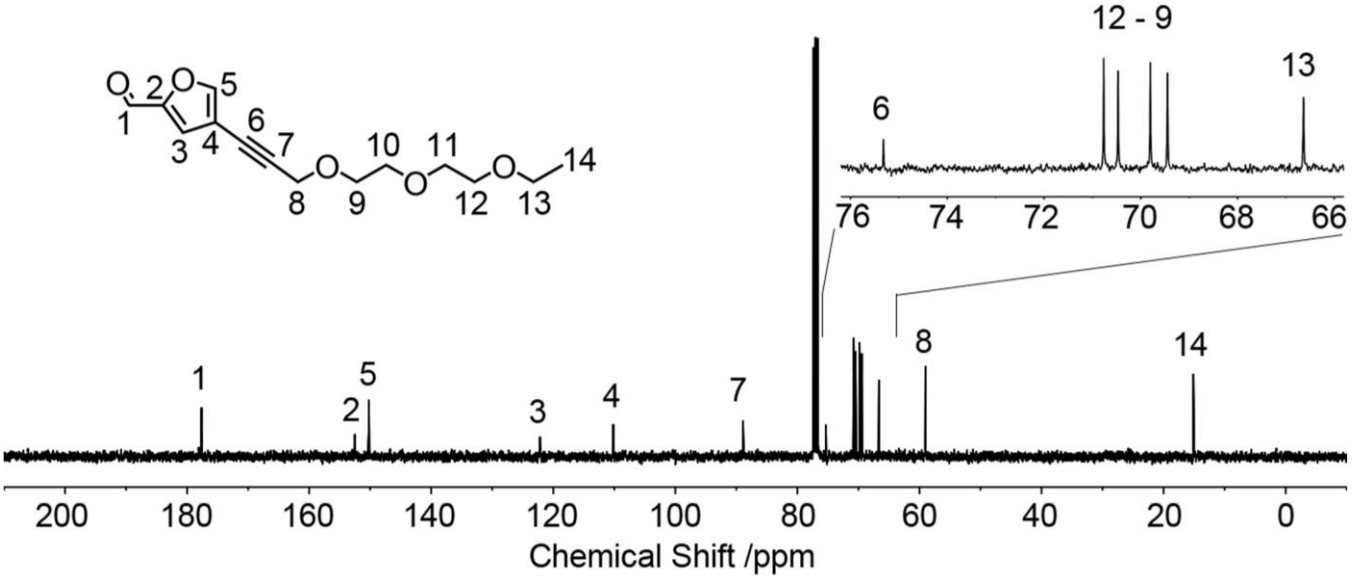
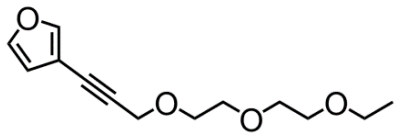


Fig. S3. ^{13}C NMR spectrum of 4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-1-propynyl)-2-furancarbaldehyde in $CDCl_3$ with corresponding assignments.



3-(3-{2-[2-(Ethoxy) ethoxy] ethoxy}-1-propynyl)-furan was synthesized in the same manner as 4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-1-propynyl)-2-furancarbaldehyde, except for 4-bromo-2-furancarbaldehyde replaced by 3-bromofuran (0.29 g, 2 mmol). The crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, *v*/*v*) to give a colorless oil (0.19 g, 39%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.39 – 7.34 (m, 1H), 6.44 (s, 1H), 4.39 (s, 2H), 3.83 – 3.46 (m, 12H), 1.21 (t, *J* = 8.9, 5.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.91, 142.77, 112.55, 107.01, 86.98, 77.53, 70.71, 70.47, 69.81, 69.17, 66.63, 59.16, 15.15.

HRMS (ESI): *m* / *z* calcd for $C_{13}H_{18}O_4$ [*M* + *Na*]$^+$: 238.1205, found: 261.1094.

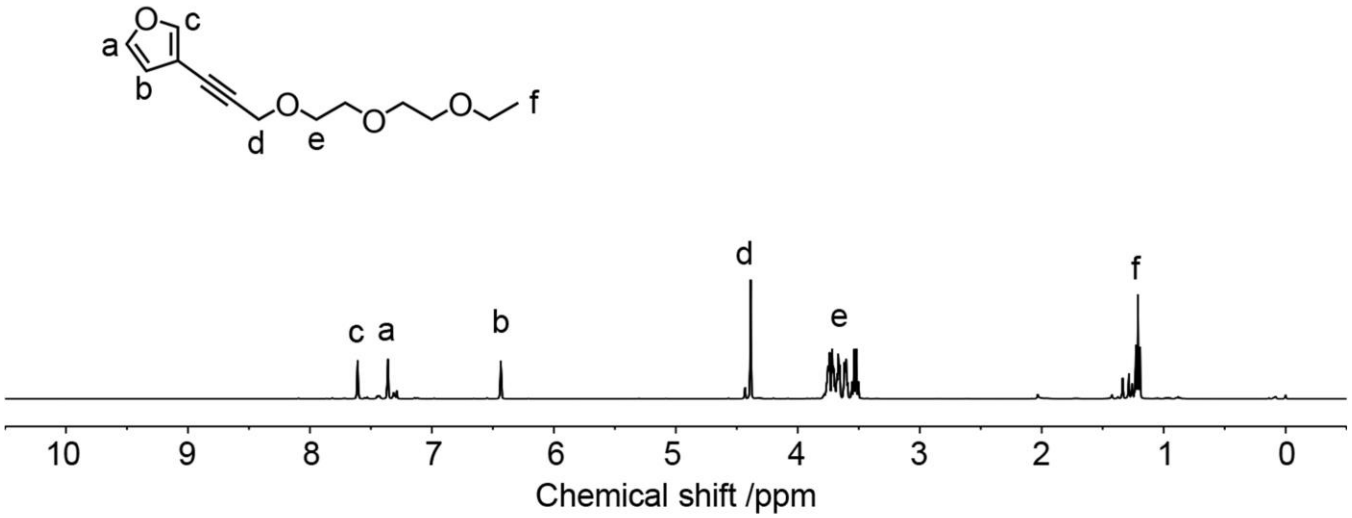


Fig. S4. ^{1}H NMR spectrum of 3-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-1-propynyl)-furan in $CDCl_3$ with corresponding assignments.

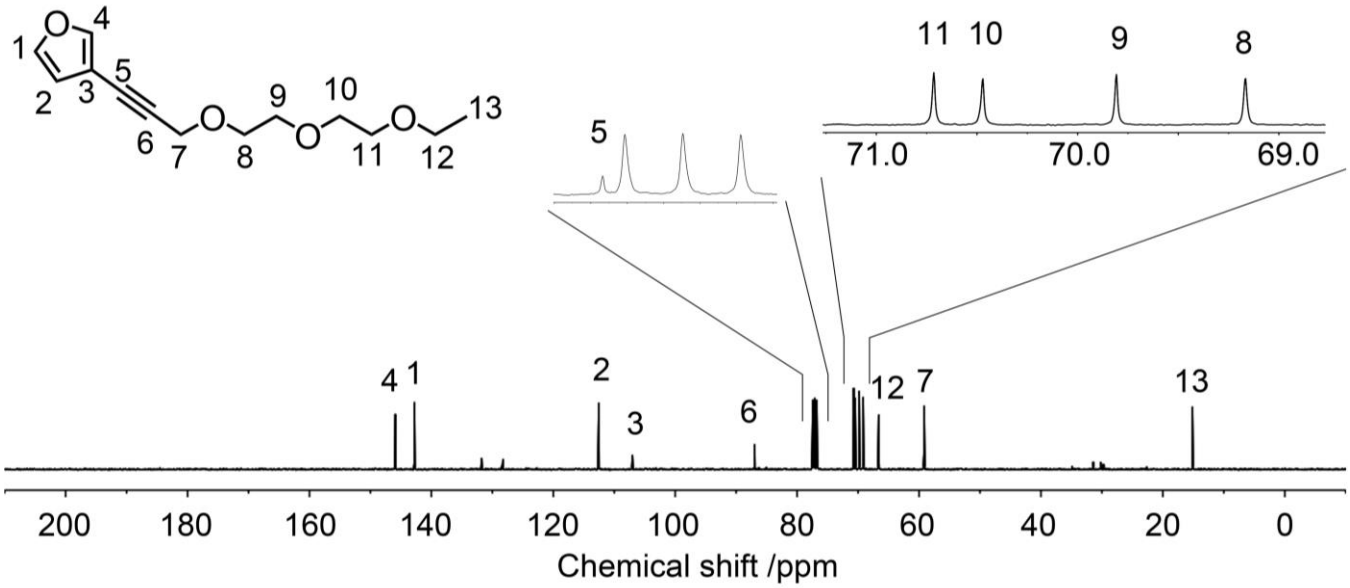
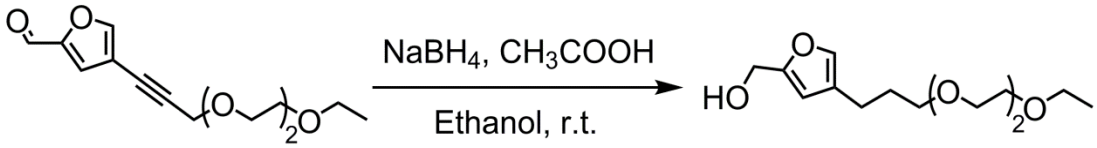


Fig. S5. ^{13}C NMR spectrum of 3-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-1-propynyl)-furan in $CDCl_3$ with corresponding assignments.



[4-(3-{2-[2-(Ethoxy) ethoxy] ethoxy}-propyl)-furan-2-yl]-methanol was synthesized according to the literature.[4] 4-(3-{2-[2-(Ethoxy) ethoxy] ethoxy}-1-propynyl)-2-furancarbaldehyde (0.6 g, 2 mmol) was dissolved in ethanol (20 mL) with stirring. The Pd/C (10%, wt) catalyst (200 mg) and acetic acid (1 mL) were added to the reaction solution. $NaBH_4$ (0.64 g, 16 mmol) was slowly added to the reaction system at 0 °C. After stirred at room temperature for 24 h, the mixture was filtered. The filtrate was washed with water (100 mL), and then extracted with ethyl acetate (30 mL) for three times. The collected organic layer was concentrated and purified with column chromatography (silica gel, ethyl acetate/petroleum ether = 1/4, *v*/*v*) to give a colorless oil (0.34 g, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 1.0 Hz, 1H), 6.18 (s, 1H), 4.55 (d, *J* = 5.1 Hz, 2H), 3.69 – 3.46 (m, 12H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.12, 138.89, 125.42, 109.27, 70.68, 70.64, 70.43, 70.18, 69.85, 66.66, 57.66, 29.82, 21.33, 15.15.

HRMS (ESI): *m / z* calcd for $C_{14}H_{24}O_5$ $[M + Na]^+$: 295.1516, found: 295.1915.

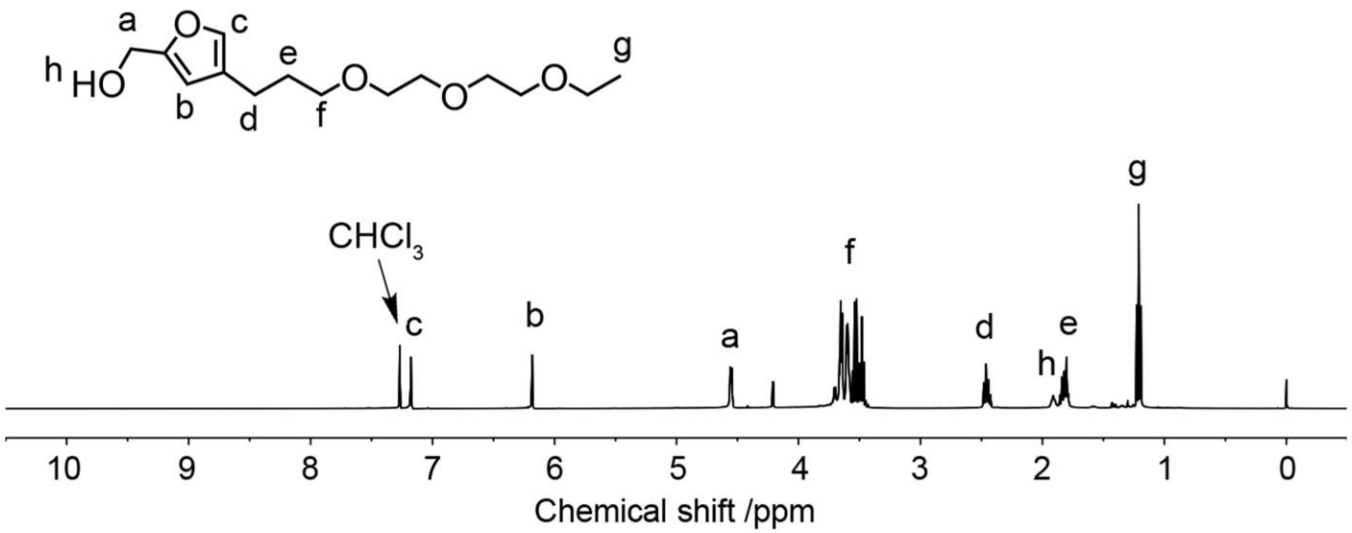


Fig. S6. ^{1}H NMR spectrum of [4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-propyl)-furan-2-yl]-methanol in $CDCl_3$ with corresponding assignments.

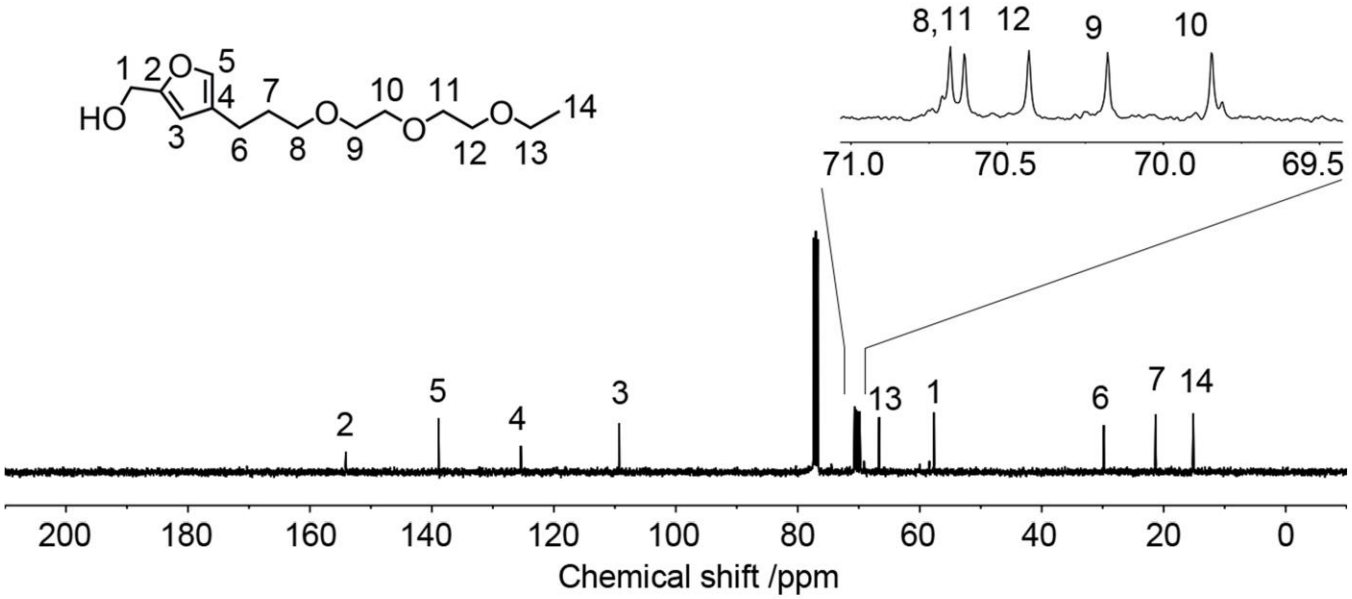
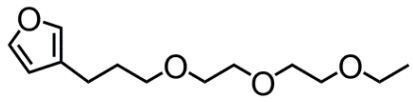


Fig. S7. ^{13}C NMR spectrum of [4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-propyl)-furan-2-yl]-methanol in $CDCl_3$ with corresponding assignments.



3-(3-{2-[2-(Ethoxy) ethoxy] ethoxy}-propyl)-furan was synthesized in the same manner as [4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-propyl)-furan-2-yl]-methanol, except for [4-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-propyl)-furan-2-yl]-methanol replaced by 3-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-1-propynyl)-furan (0.55 g, 2 mmol). The crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether = 1/4, *v*/*v*) to give a colorless oil (0.45 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 1H), 7.22 (s, 1H), 6.27 (s, 1H), 3.68 – 3.46 (m, 12H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.69, 138.91, 124.49, 111.01, 70.70, 70.62, 70.46, 70.17, 69.85, 66.64, 29.89, 21.25, 15.17.

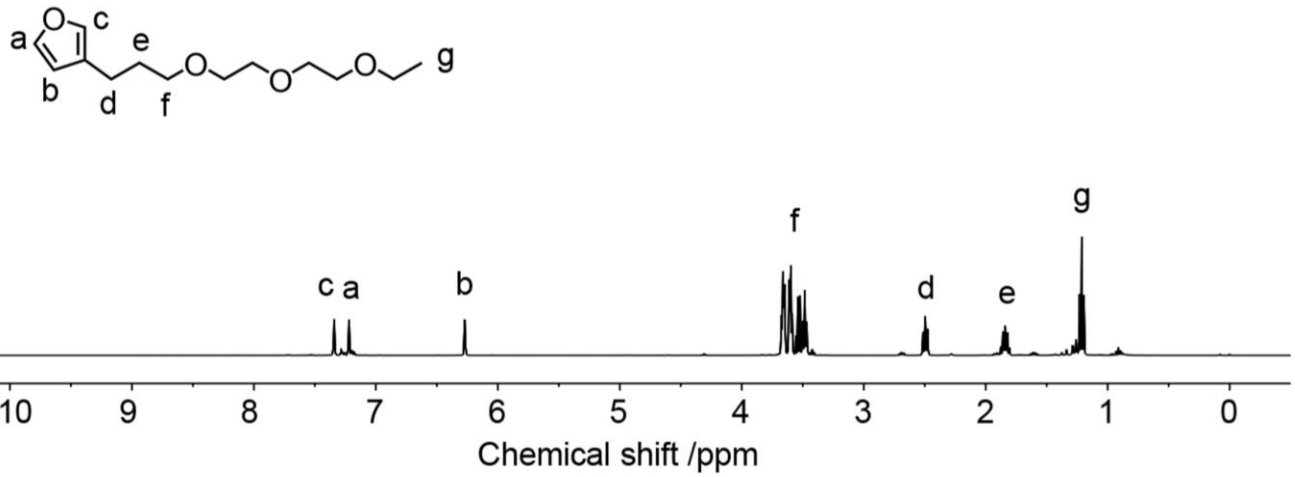


Fig. S8. ^{1}H NMR spectrum of 3-(3-{2-[2-(ethoxy) ethoxy] ethoxy}-propyl)-furan in $CDCl_3$ with corresponding assignments.

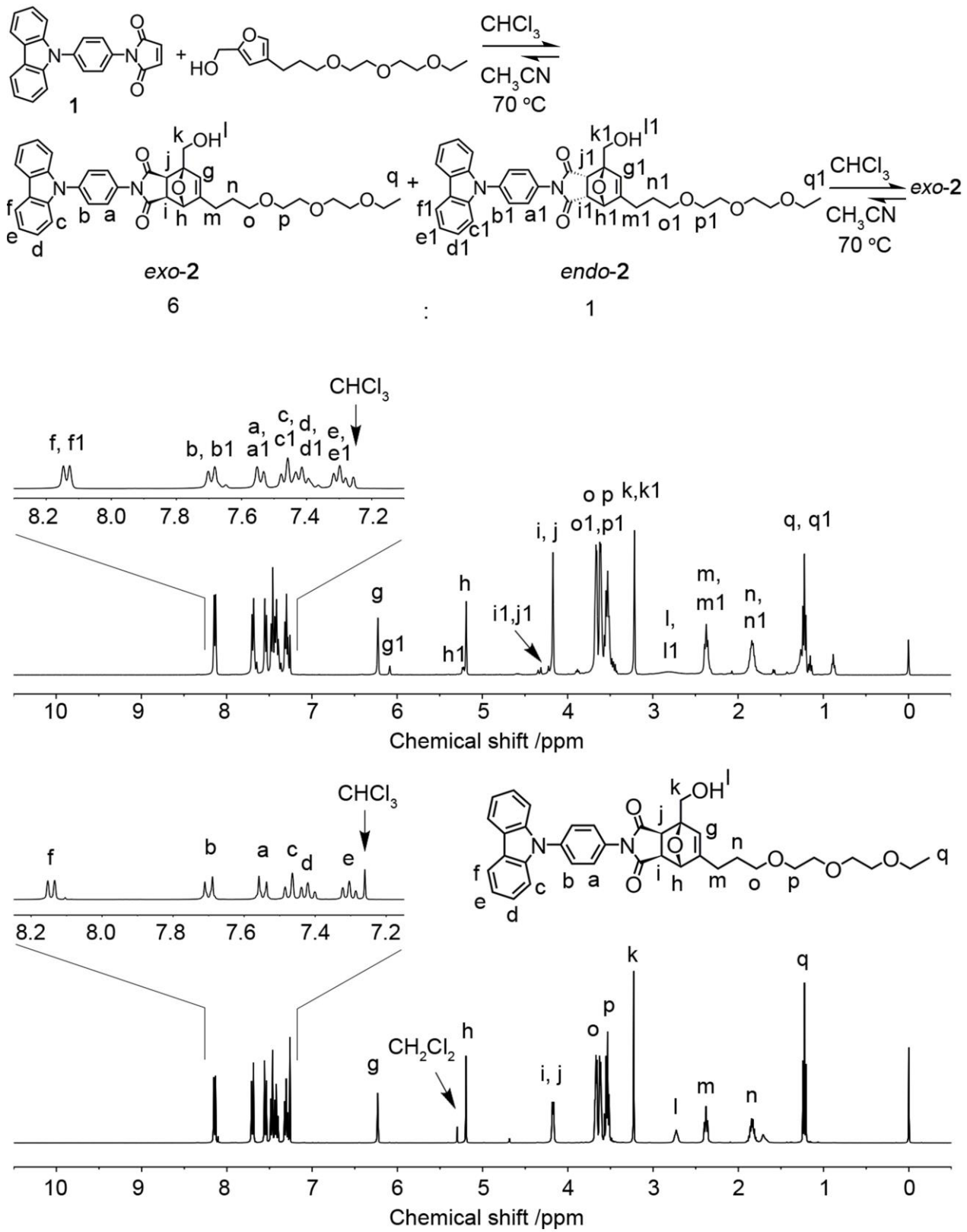


Fig. S9. ^{1}H NMR spectra of initially formed mixture of kinetically favored *endo*-**2** and thermodynamically stable *exo*-**2** (top) and finally pure *exo*-**2** (bottom) in $CDCl_3$ with corresponding assignments.

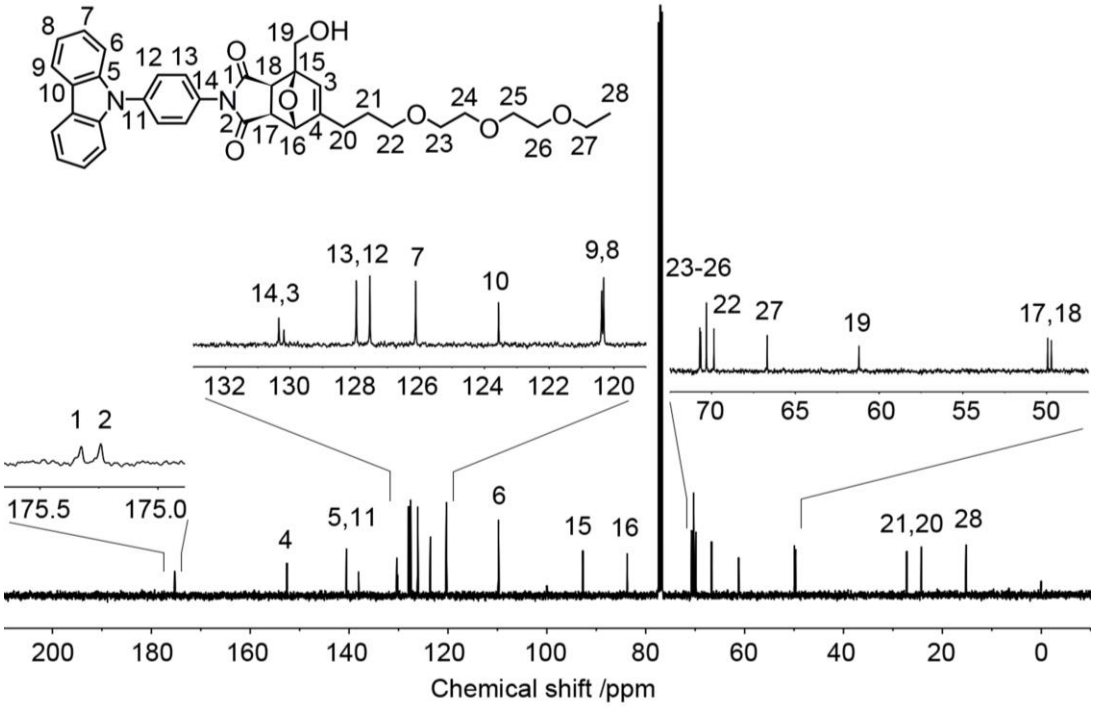


Fig. S10. ^{13}C NMR spectrum of **2** in $CDCl_3$ with corresponding assignments.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1600 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

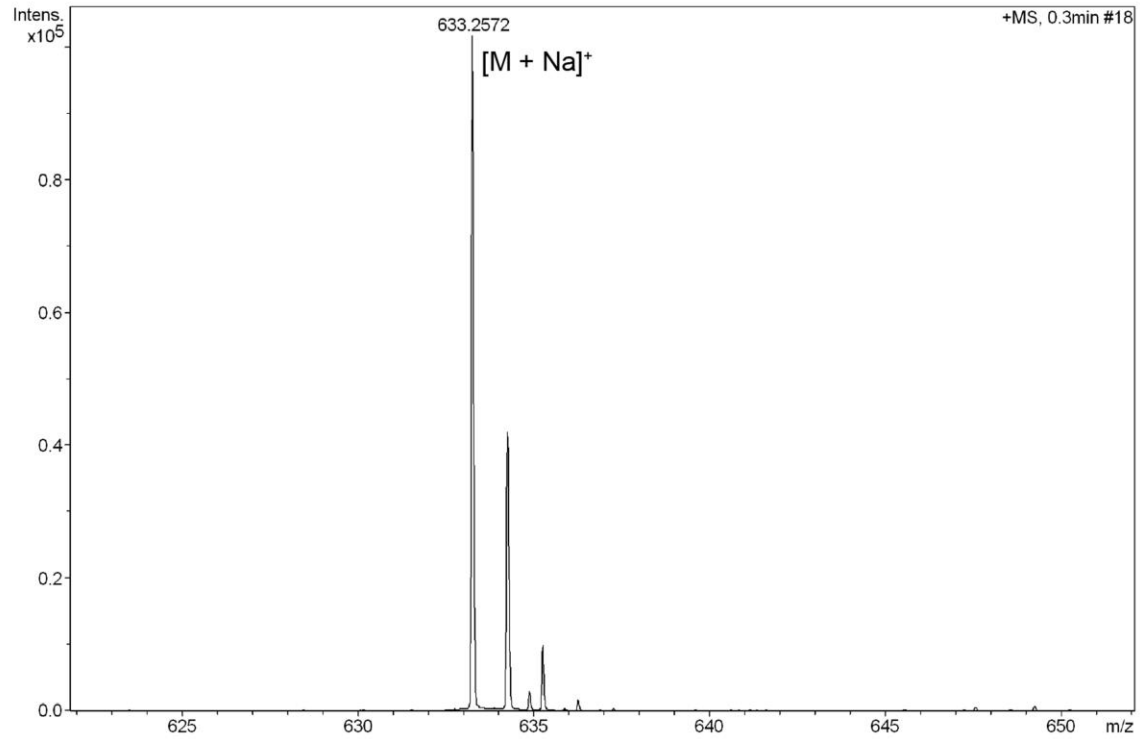


Fig. S11. High-resolution mass spectrum of **2**.

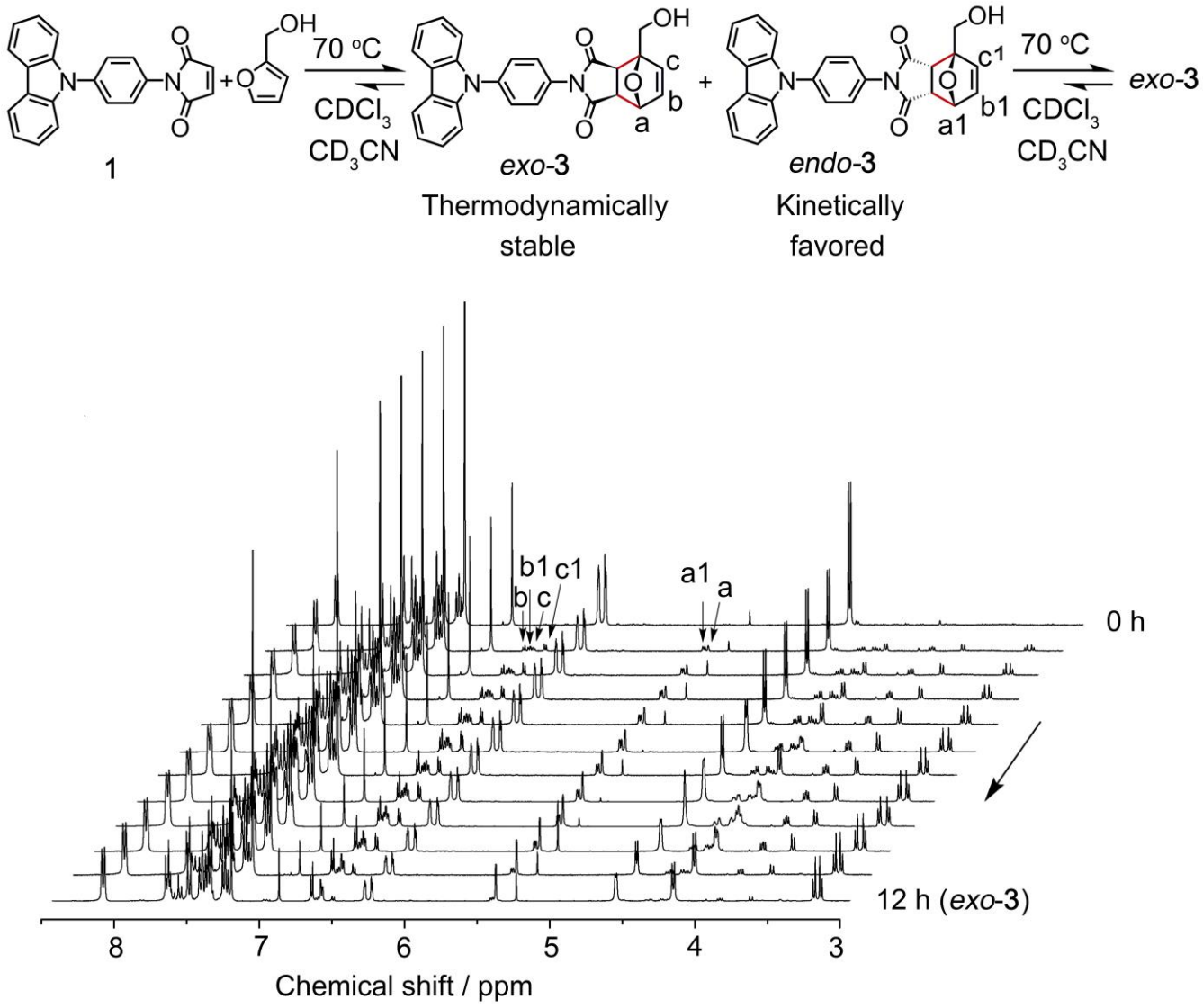


Fig. S12. ^{1}H NMR spectra from initially formed mixture of *endo*-**3** and *exo*-**3,** to finally *exo*-**3** in $CDCl_3$.

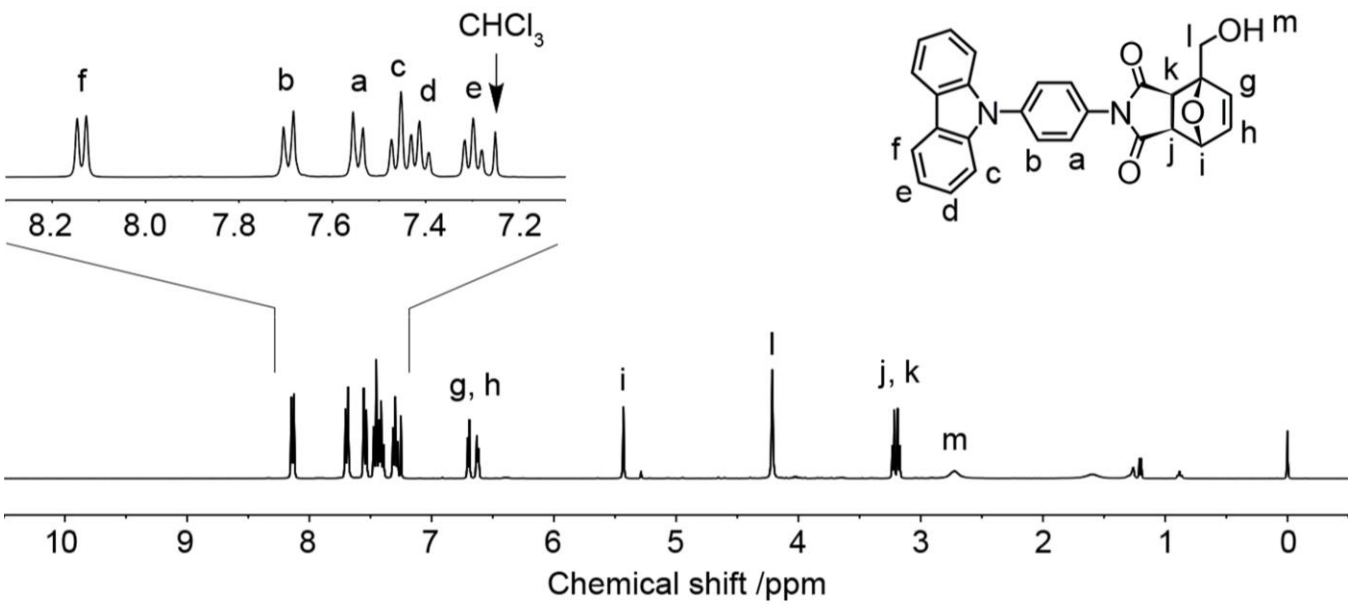


Fig. S13. ^{1}H NMR spectrum of **3** in $CDCl_3$ with corresponding assignments.

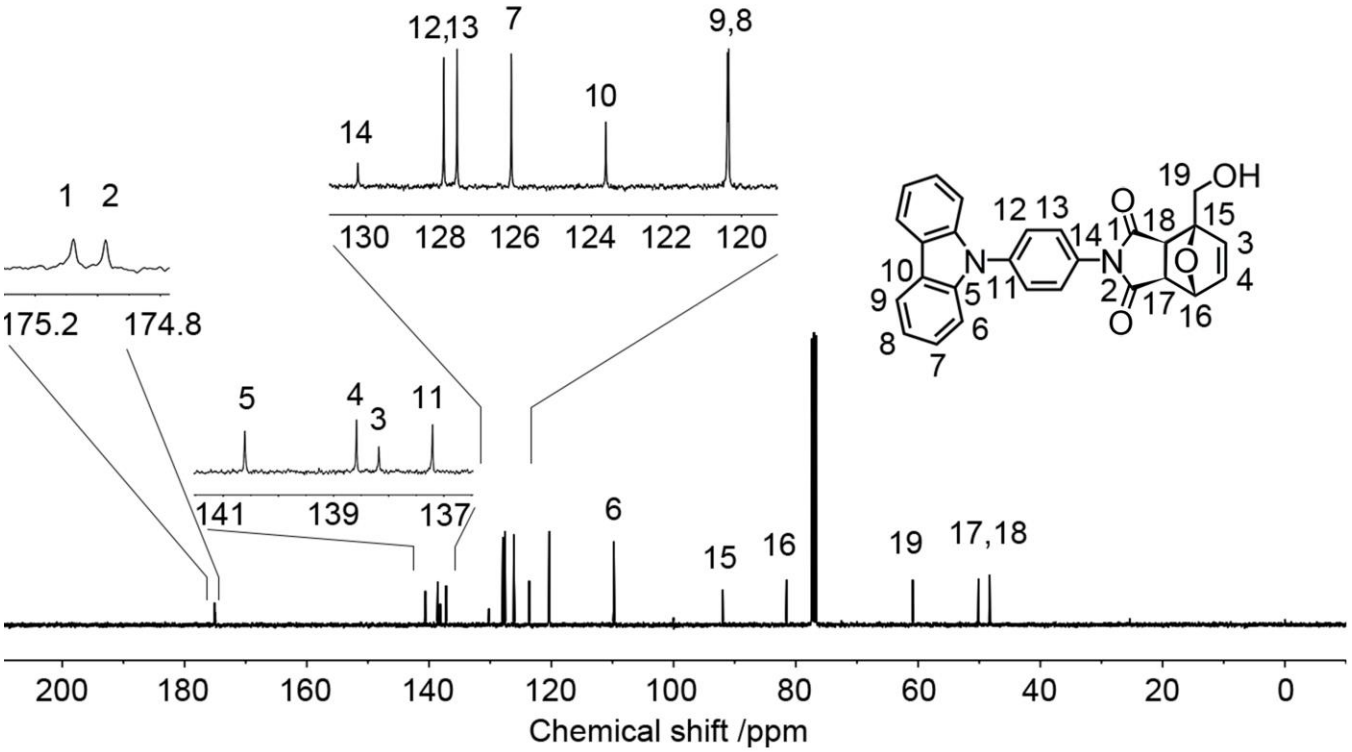


Fig. S14. ^{13}C NMR spectrum of **3** in $CDCl_3$ with corresponding assignments.

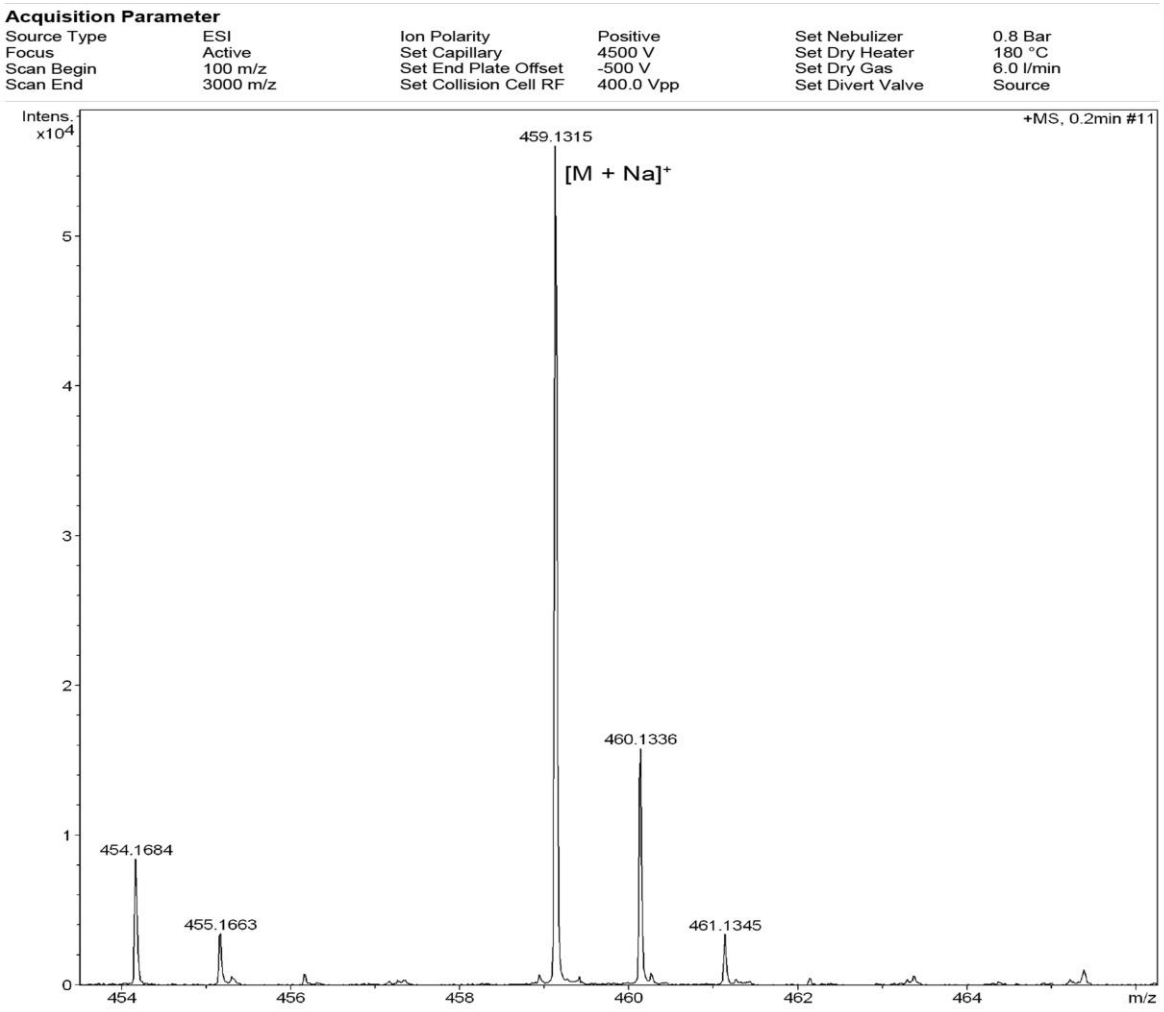


Fig. S15. High-resolution mass spectrum of **3**.

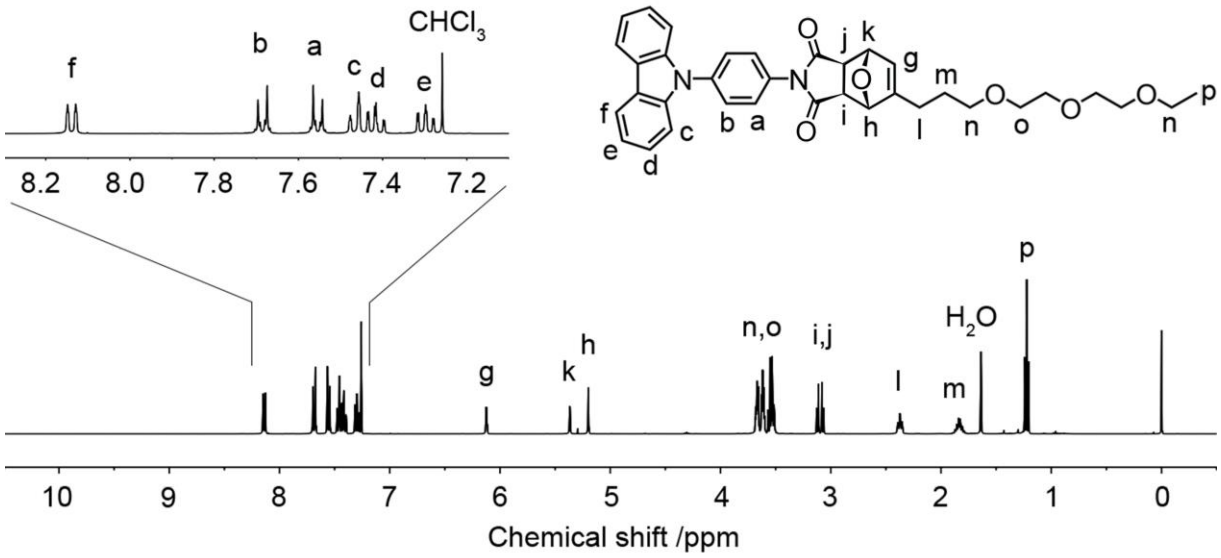


Fig. S16. ^{1}H NMR spectrum of **4** in $CDCl_3$ with corresponding assignments.

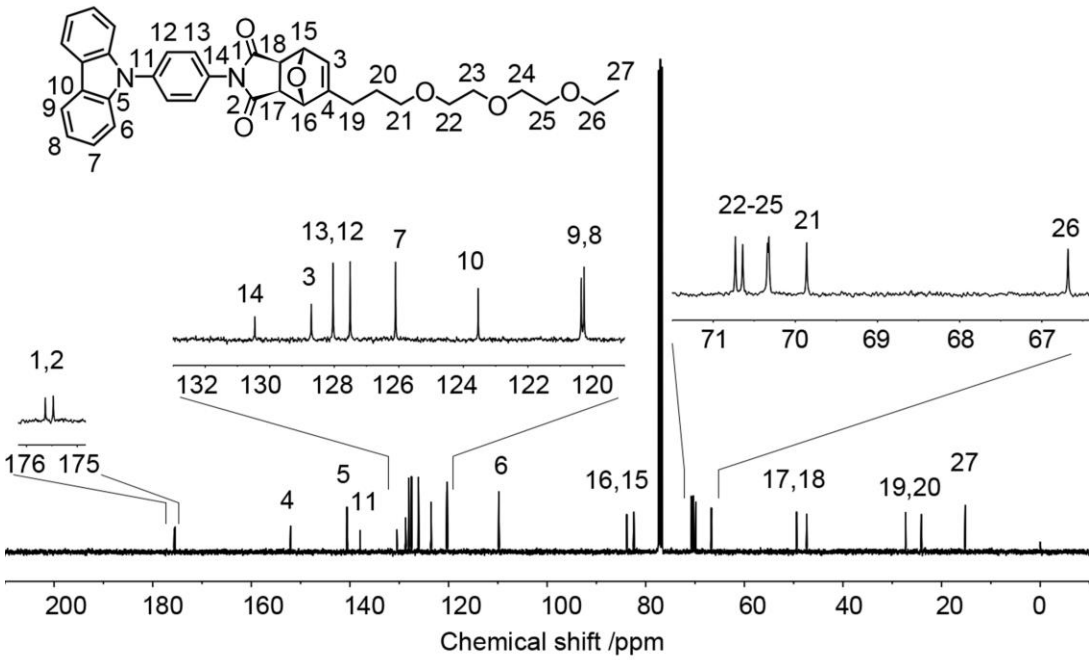


Fig. S17. ^{13}C NMR spectrum of **4** in $CDCl_3$ with corresponding assignments.

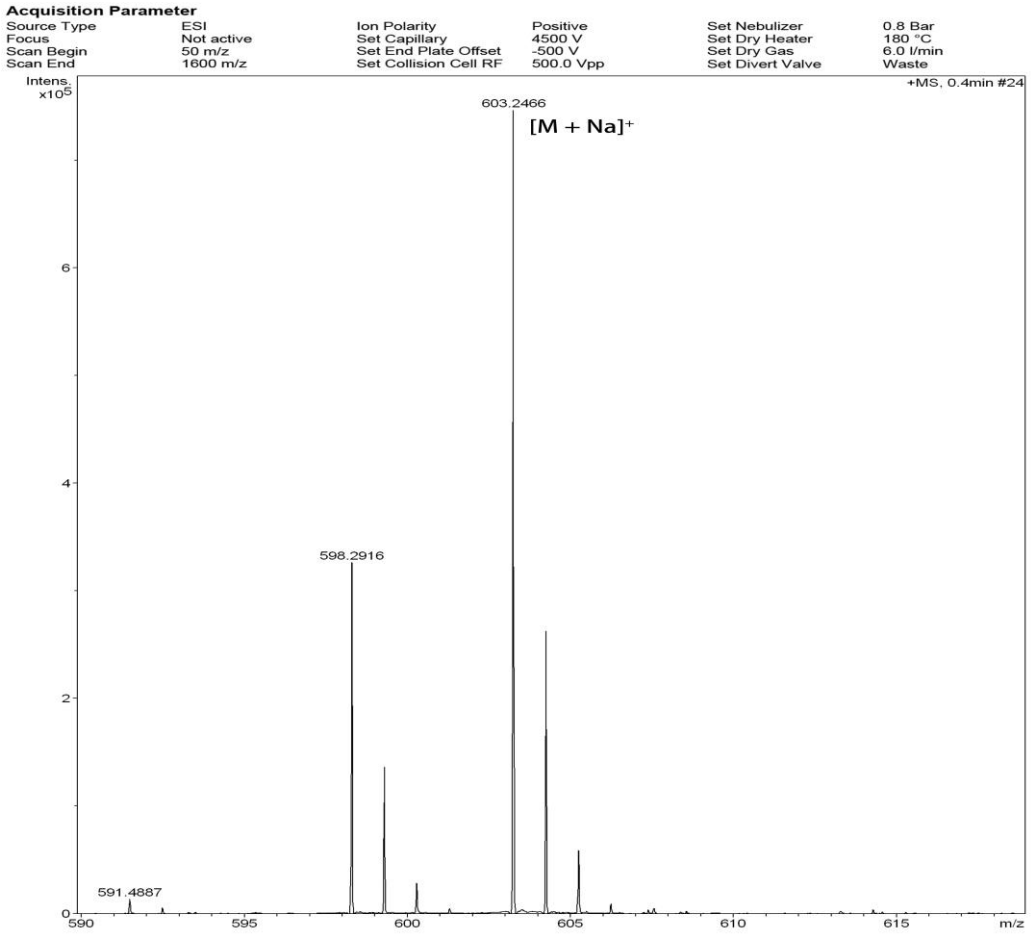


Fig. S18. High-resolution mass spectrum of **4**

3. Fluorescence spectroscopy

Steady-state fluorescence spectroscopy

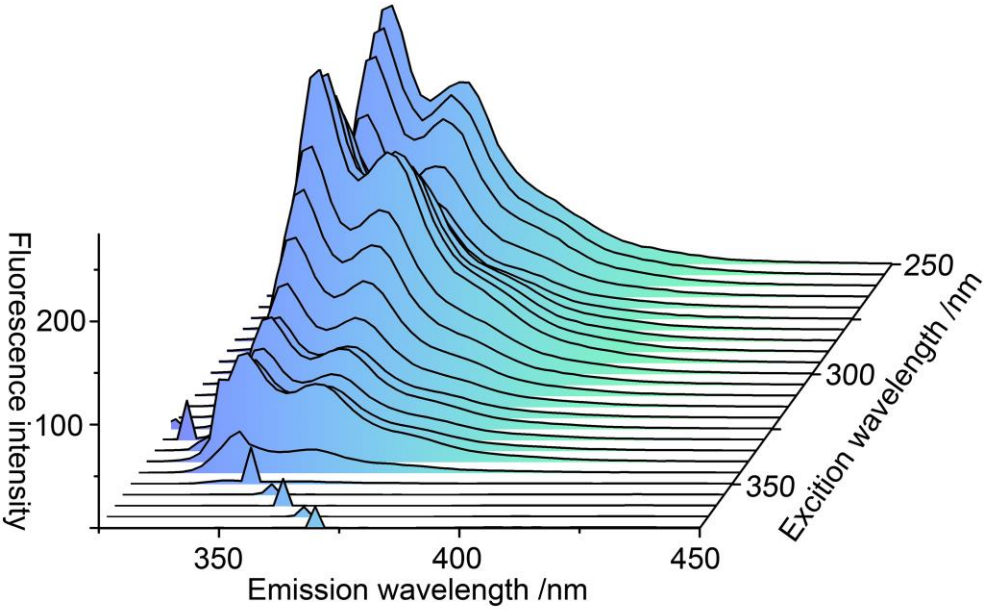


Fig. S19. Three-dimensional fluorescence spectra of **4** in dichloromethane. [**4**] = 2×10^{-5} M.

Time-resolved fluorescence spectroscopy

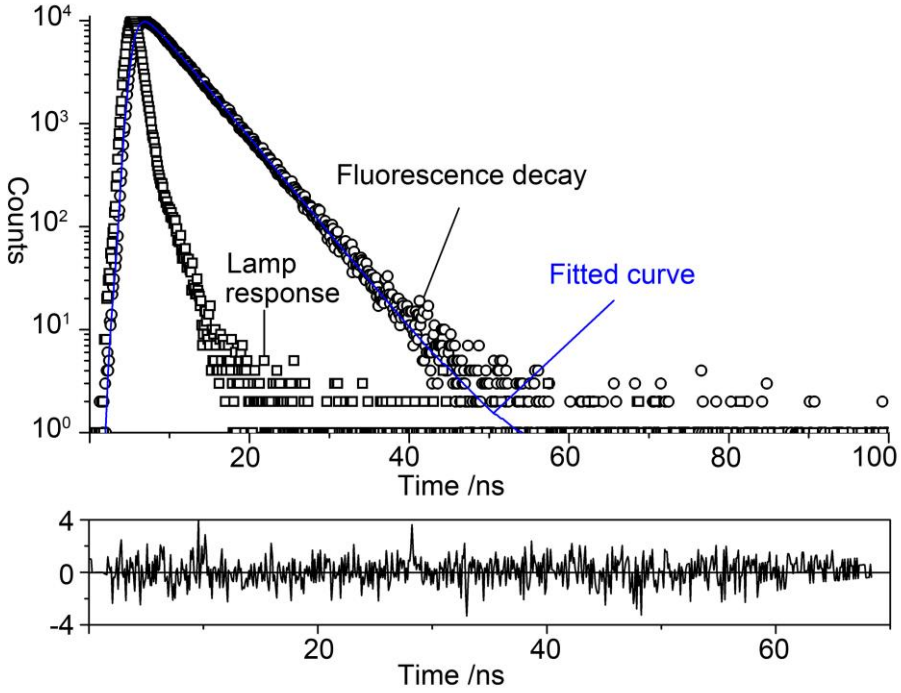
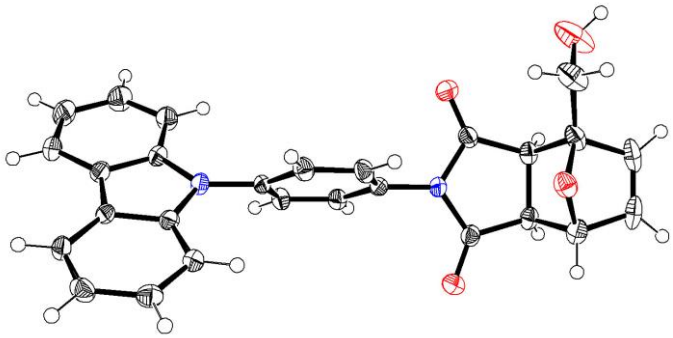


Fig. S20. Fluorescence decay of **4** in dichloromethane, $<\tau>$ = 4.6 ns χ^2 = 0.993. λ_{ex} = 295 nm, λ_{em} = 345 nm. [**4**] = 2×10^{-5} M.

4. Single-crystal X-ray diffraction analysis

Table S1. Crystal data and structure refinement for **3**.



Identification code	P150428F
Empirical formula	$C_{27}H_{20}N_2O_4$
Formula weight	436.45
Temperature	162 (30) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	$P2_1/c$
Unit cell dimensions	a= 13.3657 (5) Å α = 90.00 ° b= 10.0390 (3) Å β = 97.407 (3) ° c = 15.8436 (5) Å γ = 90.00 °
Volume	2108.12 (12) Å ^{3}
Z	4
Calculated density	1.375 Mg/m^3
Absorption coefficient	0.093 mm^{-1}
F (000)	912
Crystal size	0.4 x 0.3 x 0.1 mm^3
Theta range for data collection	4.0240 to 28.3880°
Limiting indices	-15<=h<=13, -11<=k<=11, -17<=l<=18
Reflections collected / unique	7907/3701 [R (int) = 0.0308]
Completeness to theta = 26.3154°	99.76%
Max. and min. transmission	1.00000 and 0.46433
Refinement method	Full matrix least square F^2
Data / restraints / parameters	3701 / 0 / 299
Goodness-of-fit on F^2	1.043
Final R indices [I > 2signma (I)]	R1 = 0.0497, wR2 = 0.1138
R indices (all data)	R1 = 0.0672, wR2 = 0.1256
Largest diff. peak and hole	0.28 and -0.25 e.Å^{-3}

5. Aggregation behaviours

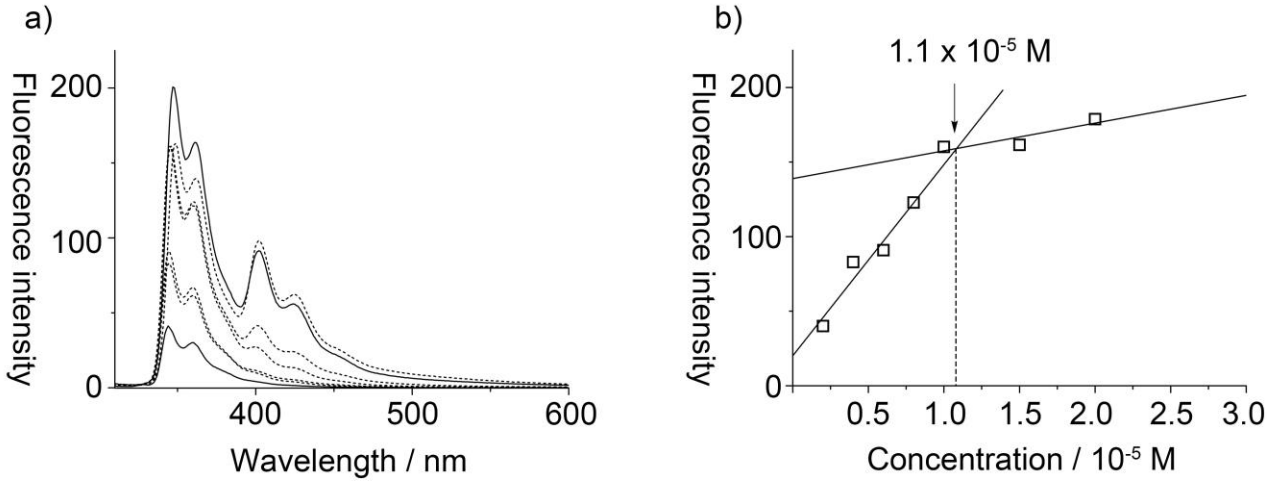


Fig. S21. a) Fluorescence spectra of **2** in deionized water-containing THF (95% water, v/v) with increasing concentration. b) The changes in fluorescence intensity at 345 nm with increasing the concentration of **2**. Arrow indicates the critical turning point at 1.1 x 10^{-5} M, which reveals a critical aggregation concentration.

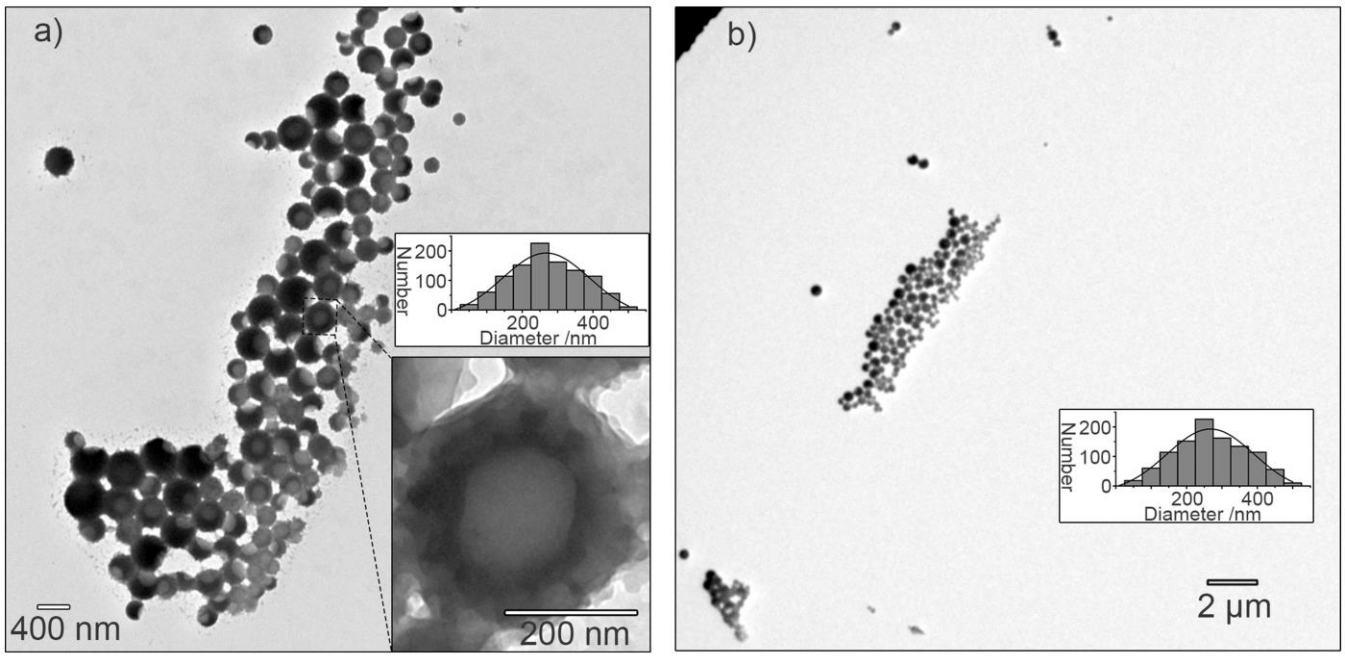


Fig. S22. a) and b) TEM images of vesicular aggregates of **2** prepared from the aqueous solution. [**2**] = 2 x 10^{-4} M. Inset: size distribution of vesicular aggregates of **2**.

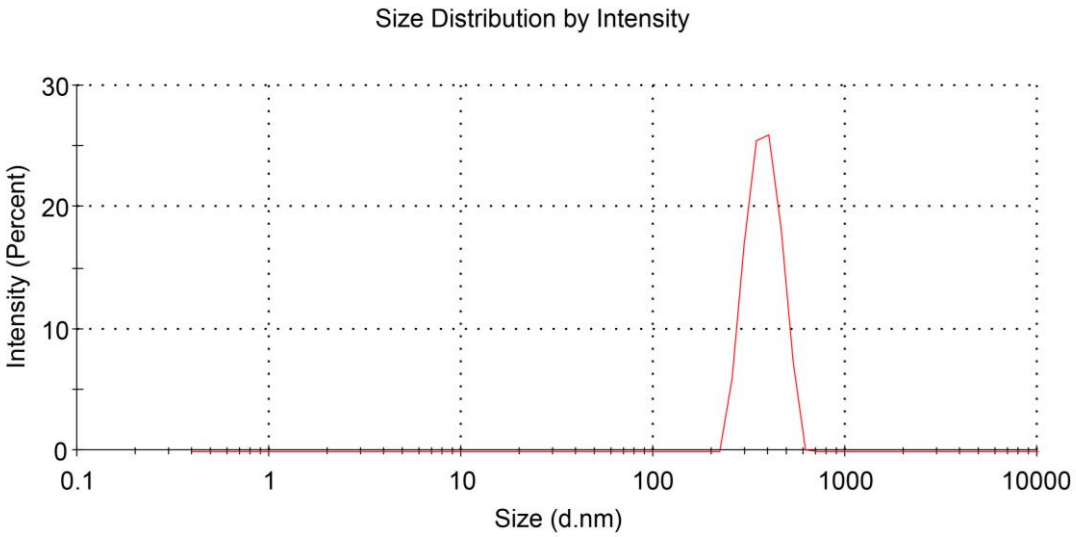


Fig. S23. Size distribution of the aggregates of **2** in water obtained from Dynamic light scattering measurements. [**2**] = 2 x 10^{-4} M.

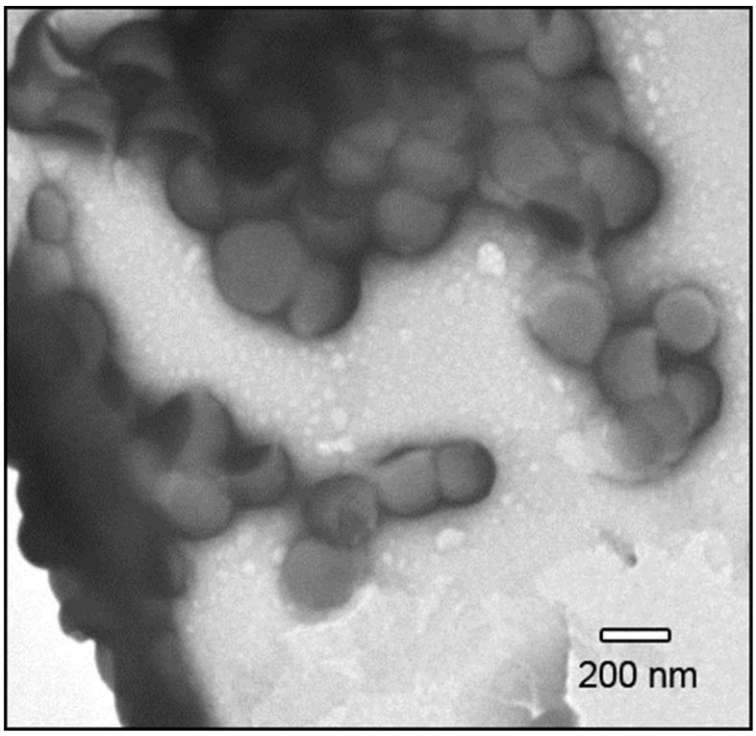


Fig. S24. TEM image of the reformed vesicular aggregates of **2** after thermal treatment of 90 ^{o}C for 2 hr, then cooling to room temperature. [**2**] = 2 x 10^{-4} M.

6. References

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