

Supporting Information for

Self-assembly of Supramolecular Light-harvesting Arrays from Symmetric Perylene-3,4-dicarboximide Trefoils

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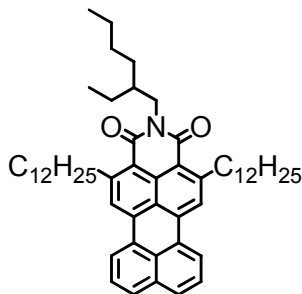
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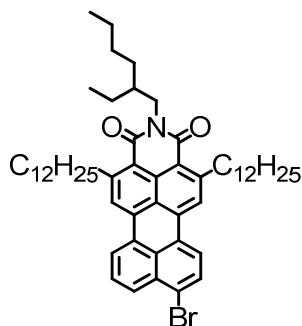
Synthesis

Reagents were purchased at reagent grade and used as received. Column chromatography was carried out with SiO₂ (particle size 0.040–0.063 mm, 230–400 mesh) and technical solvents. Size exclusion chromatography was performed with Bio-Beads S-X1 from Bio-Rad Laboratories, Inc. ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE III 500 spectrometer. Chemical shifts were reported in ppm relative to the signal of Si(CH₃)₄. Residual solvent signals in the NMR spectra were used as an internal reference. Coupling constants (*J*) were given in Hz. The apparent resonance multiplicity was described as s (singlet), d (doublet), t (triplet), and m (multiplet). MALDI-MS were measured on a Bruker Autoflex III

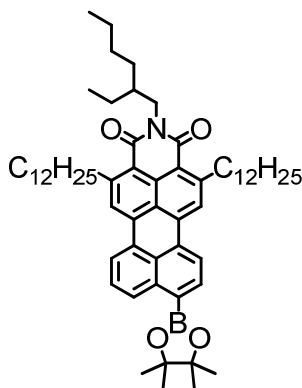
MALDI-TOF mass spectrometer using 2-hydroxy-1-naphthoic acid or dithranol as a matrix, and high-resolution HR-ESI-MS spectra on an Agilent 6210 LC-TOF; signals are reported in m/z units. The synthesis of **P1**¹ and 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene² have been reported previously.



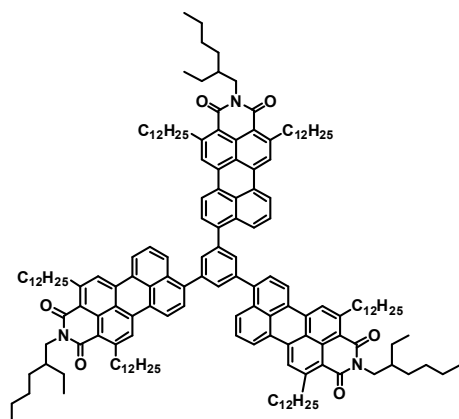
P2. To a stirring solution of **P1** (0.610 g, 1.407 mmol) and 1-dodecene (3.12 mL, 14.07 mmol) in mesitylene (28 mL) that had been purged with N_2 was added $Ru(H_2)CO(PPh_3)_3$ (0.155 g, 0.169 mmol). The solution was heated at reflux and stirred under N_2 for 2 d. The solvent was evaporated to afford a dark orange solid. Column chromatography with CH_2Cl_2 /hexanes (4:1) followed by drying under high vacuum afforded the product as an orange solid (0.986 g, 91%). 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.19 (d, J = 7.5 Hz, 2H), 7.91 (s, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.49 (apparent t, J = 7.8 Hz, 2H), 4.13 (d, J = 7.5 Hz, 2H), 3.43–3.38 (m, 4H), 2.01–1.88 (m, 1H), 1.77–1.63 (m, 4H), 1.57–1.20 (m, 44H), 0.96–0.88 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 163.90, 150.51, 134.78, 133.88, 132.07, 130.07, 128.88, 127.58, 126.64, 124.29, 124.10, 122.85, 117.85, 43.67, 37.61, 37.26, 31.93, 31.10, 30.57, 30.17, 29.74, 29.73, 29.70, 29.67, 29.38, 28.55, 23.89, 23.24, 22.69, 14.13, 10.73; HR-ESI-MS: m/z 770.5863 ($[M + H]^+$, calcd for $C_{54}H_{76}NO_2$: 770.5871).



P3. To a stirring solution of **P2** (0.963 g, 1.25 mmol) in CH_2Cl_2 (100 mL) was added Br_2 (0.068 mL, 1.31 mmol) dropwise. The mixture was stirred at reflux for 2 h and then washed with $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ and H_2O . The mixture was concentrated under reduced pressure, and the crude material was passed through a pad of silica with CH_2Cl_2 . Evaporation of the filtrate afforded the product as an orange solid (0.858 g, 81%). ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 8.26 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.98 (s, 1H), 7.92 (s, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.63–7.56 (m, 1H), 4.15 (d, J = 7.5 Hz, 2H), 3.42–3.38 (m, 4H), 1.98–1.94 (m, 1H), 1.79–1.63 (m, 4H), 1.52–1.15 (m, 44H), 0.96–0.88 (m, 12H); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C): δ = 163.83, 150.72, 150.64, 134.18, 134.05, 132.49, 131.98, 130.82, 129.35, 129.19, 128.80, 128.78, 127.80, 125.25, 124.67, 124.37, 123.92, 123.54, 122.93, 118.31, 118.29, 43.75, 37.61, 37.24, 31.93, 31.14, 30.58, 30.16, 29.73, 29.70, 29.67, 29.38, 28.55, 23.91, 23.23, 22.70, 14.14, 14.10, 10.74; HR-ESI-MS: m/z 870.4782 ($[M + \text{Na}]^+$, calcd for $\text{C}_{54}\text{H}_{74}^{79}\text{BrNNaO}_2$: 870.4795).

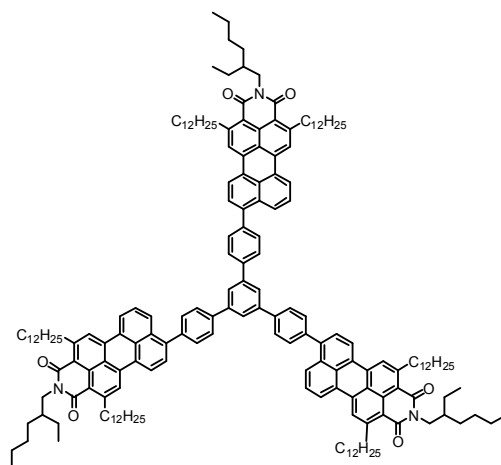


P4. Pd(dppf)Cl₂·CH₂Cl₂ (0.048 g, 0.059 mmol) and potassium acetate (0.306 g, 3.12 mmol) were added to a solution of **P3** (0.100 g, 0.118 mmol) and bis(pinacolato)diboron (0.345 g, 1.36 mmol) in 1,4-dioxane (12 mL). The solution was purged with N₂, and stirred at reflux for 14 h under N₂. The cooled mixture was extracted with CH₂Cl₂ and H₂O, and the combined organic layers were dried over Na₂SO₄ and concentrated. Column chromatography with CH₂Cl₂/hexanes (1:1) afforded the product (0.090 g, 85%). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.84 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.42 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.36 (d, *J* = 7.6 Hz, 1H), 8.18–8.14 (m, 3H), 7.66 (t, *J* = 7.9 Hz, 1H), 4.17 (d, *J* = 7.5 Hz, 2H), 3.52–3.40 (m, 4H), 2.00–1.93 (m, 1H), 1.80–1.69 (m, 4H), 1.55–1.17 (m, 44H), 1.46 (s, 12H), 0.95–0.86 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ = 164.08, 150.92, 150.77, 137.83, 136.13, 135.44, 134.97, 132.22, 131.74, 131.02, 128.99, 127.65, 127.11, 125.02, 124.52, 122.96, 122.02, 118.42, 117.87, 84.11, 43.71, 37.59, 37.26, 31.92, 31.20, 30.59, 30.15, 29.72, 29.68, 29.66, 29.57, 29.37, 29.32, 28.56, 25.60, 24.99, 23.92, 23.21, 22.69, 14.13, 14.07, 10.75; HR-ESI-MS: *m/z* 895.6711 ([*M* + H]⁺, calcd for C₆₀H₈₇BNO₄: 895.6759).



1. Pd(PPh₃)₄ (0.008 g, 0.007 mmol) was added to a deaerated solution of **P3** (0.062 g, 0.073 mmol), 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (0.010 g, 0.022 mmol), and Na₂CO₃ (0.014 g, 0.132 mmol) in a mixture of toluene (2.5 mL), EtOH (1 mL) and H₂O (0.75 mL). The solution was stirred at 80 °C for 2 d. The mixture was extracted with CHCl₃ and H₂O. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated. Column chromatography with CH₂Cl₂/hexanes (1:1) yielded the product as a red solid (0.037 g, 71%).

¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.50 (d, *J* = 8.0, 2.4 Hz, 3H), 8.46 (d, *J* = 7.8 Hz, 3H), 8.26 (d, *J* = 8.4 Hz, 3H), 8.19 (s, 3H), 8.17 (s, 3H), 7.89 (s, 3H), 7.78 (d, *J* = 7.8, 3H), 7.69–7.61 (m, 3H), 4.16 (d, *J* = 7.4 Hz, 6H), 3.48–3.43 (m, 12H), 2.01–1.62 (m, 15H), 1.56–1.20 (m, 132H), 0.95–0.85 (m, 36H); ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ = 164.02, 151.92, 150.94, 141.37, 140.78, 134.84, 132.35, 129.71, 129.16, 128.46, 127.20, 124.58, 124.52, 122.83, 118.32, 43.75, 37.51, 37.24, 31.87, 31.83, 30.07, 29.94, 29.61, 29.56, 29.40, 29.36, 29.33, 29.27, 29.07, 28.85, 28.73, 28.60, 28.45, 23.80, 23.58, 22.64, 14.14, 14.02, 10.63; MALDI-MS: *m/z* 2381.257 ([*M* + H]⁺, calcd for C₁₆₈H₂₂₆N₃O₆: 2381.747).



2. Pd(PPh₃)₄ (0.0043 g, 0.0037 mmol) was added to a deaerated solution of **P4** (0.035 g, 0.039 mmol), 1,3,5-tris(4-bromophenyl)benzene (0.0067 g, 0.0124 mmol), and Na₂CO₃ (0.0081 g, 0.0760 mmol) in a mixture of toluene (1.50 mL), EtOH (0.60 mL) and H₂O (0.45 mL). The solution was stirred at 80 °C for 2 d. The mixture was extracted with CHCl₃ and H₂O. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated. Column chromatography with CHCl₃/hexanes (4:1) afforded the product as a red solid (0.011 g, 34%).
¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.55 (d, *J* = 8.2 Hz, 3H), 8.52 (d, *J* = 8.2 Hz, 3H), 8.27 (s, 3H), 8.26 (s, 3H), 8.10 (d, *J* = 8.4 Hz, 3H), 8.08 (s, 3H), 7.98 (d, *J* = 8.0 Hz, 3H), 7.61–7.45 (m, 15H), 4.19 (d, *J* = 7.5 Hz, 6H), 3.55–3.50 (m, 12H), 2.10–1.20 (m, 147H), 0.98–0.70 (m, 36H); ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ = 164.02, 150.85, 140.37, 132.30, 130.58, 129.90, 129.62, 128.40, 128.01, 127.39, 126.87, 124.59, 122.79, 118.11, 43.71, 37.52, 37.20, 31.83, 31.14, 30.50, 30.06, 29.61, 29.57, 29.42, 29.27, 29.22, 29.13, 29.01, 28.47, 23.82, 23.13, 23.08, 22.60, 14.11, 14.04, 10.65; MALDI-MS: *m/z* 2609.394 ([*M* + H]⁺, calcd for C₁₈₆H₂₃₈N₃O₆: 2609.841).

Additional SAXS/WAXS Models

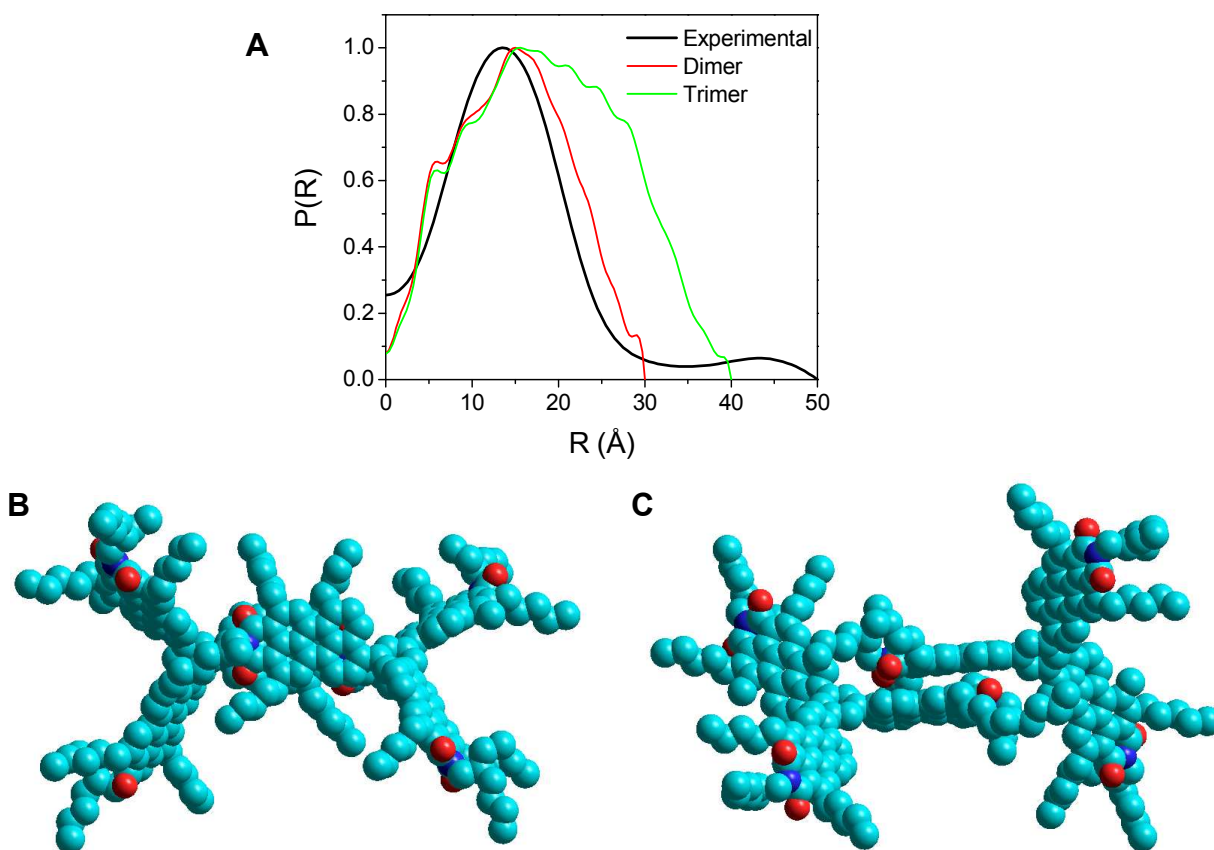


Figure S1. A) Pair-distance distribution function (PDF) of the experimental data of **1** compared with the PDFs calculated based on the structural models with varying numbers of partially stacked molecules. B) Top view of the dimer structure of two partially π -stacked **1**, where only one PMI stacks with one PMI of an adjacent monomer. C) Side view of the dimer structure of two partially π -stacked **1**, where only one PMI stacks with one PMI of an adjacent monomer. Hydrogen atoms are omitted for clarity.

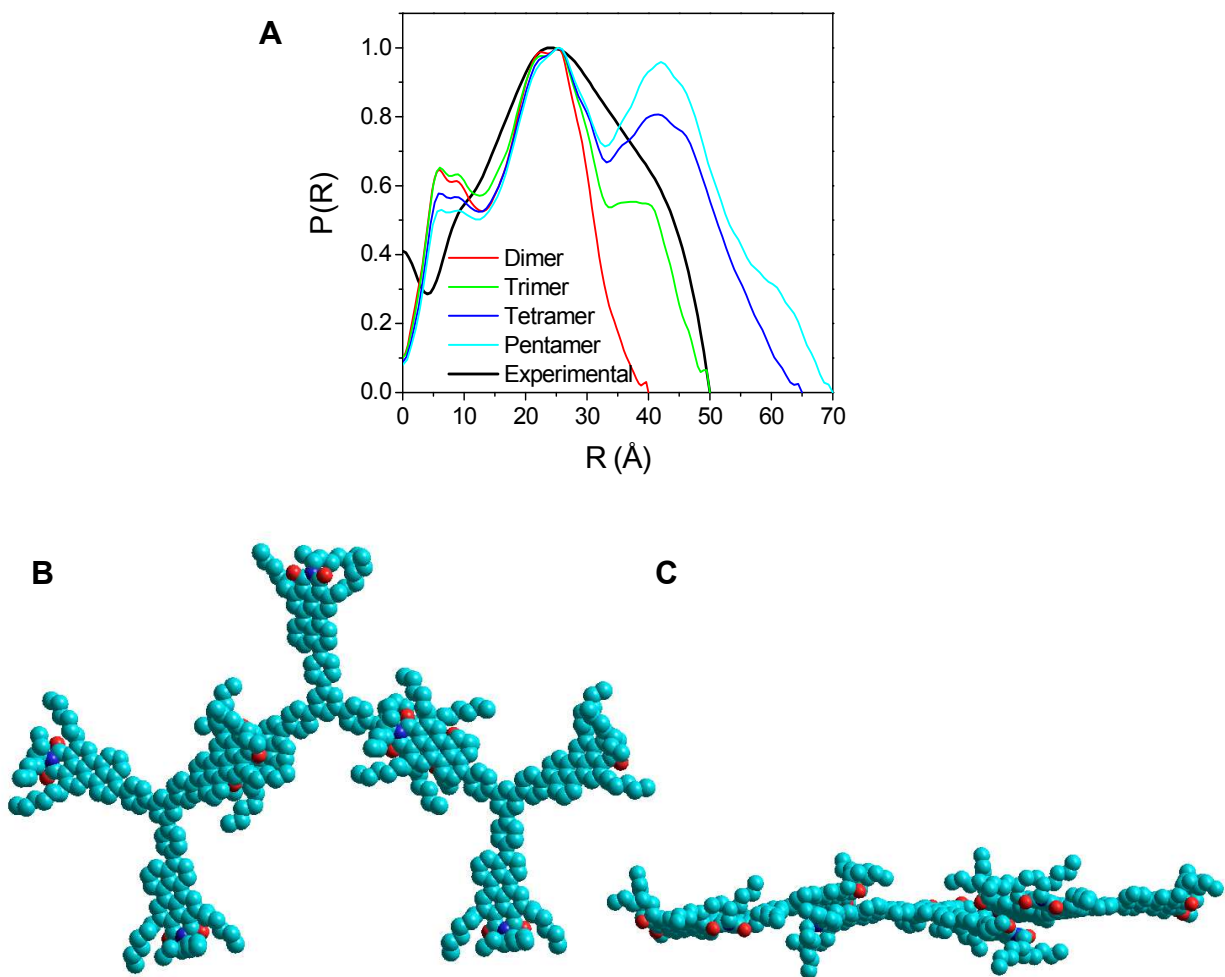


Figure S2. A) Pair-distance distribution function (PDF) of the experimental data of **2** compared with the PDFs calculated based on the structural models with varying numbers of partially stacked molecules. B) Top view of the trimer of three partially π -stacked **2**, where one PMI from each monomer overlaps with an adjacent molecule. C) Side view of the trimer of three partially π -stacked **2**, where one PMI from each monomer overlaps with an adjacent molecule. Hydrogen atoms are omitted for clarity.

Time-resolved Fluorescence Spectra in THF and MCH

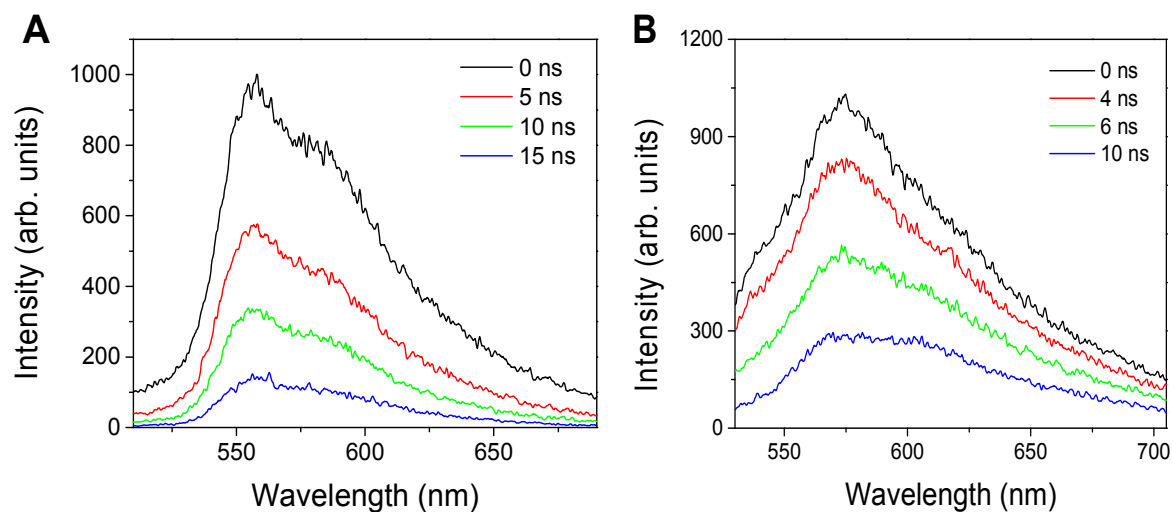


Figure S3. Time-resolved fluorescence spectra of **1** in (A) THF (1×10^{-4} M) and (B) MCH (6×10^{-4} M) following 390 nm, 100-fs pulsed excitation.

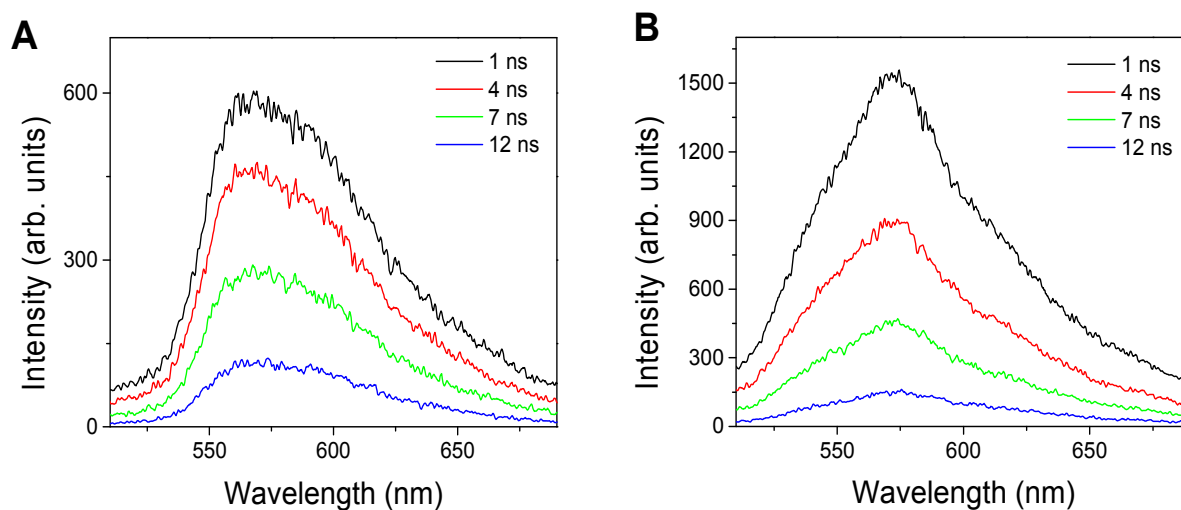


Figure S4. Time-resolved fluorescence spectra of **2** in (A) THF (1×10^{-4} M) and (B) MCH (1×10^{-3} M) following 390 nm, 100-fs pulsed excitation.

References

- (1) Keerthi, A.; Liu, Y.; Wang, Q.; Valiyaveetil, S. *Chem. Eur. J.* **2012**, *18*, 11669–11676.
- (2) Biqing, B.; Yuwen, L.; Zhan, X.; Wang, L. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3431–3439.