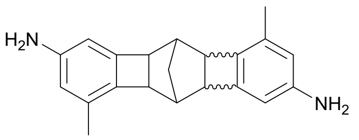
Materials.

4-((Trimethylsilyl)ethynyl)benzaldehyde (Wako, 97%), 4-bromo-3-methylaniline (TCI, 98%), norbornadiene (NBD) (TCI, 97%), Cs_2CO_3 (Wako, 95%-102%), $Pd(OAc)_2$ (Wako, 97%), PPh_3 (Wako, 97%), 1,4-dioxane (super hydrated, 99.5%), 2-azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMP) (TCI, 97%), 4-dimethylaminopyridine (DMAP) (Wako, 97%), CuBr (Sigma-aldrich, 98%), *N,N,N',N'',N''*-pentamethyldiethylene-triamine (PMEDTA) (Wako, 98%), benzil (TCI, 99%), CH_3COONH_4 (Wako, 95%), $K_3[Fe(CN)_6]$ (Wako, 99%), KOH (Wako, 85%), poly(ethylene glycol) methyl ether (M_n~2000) (Aldrich), 4-toluenesulfonyl chloride (TCI, 99%), anisole(anhydrous) (Aldrich, 99.7%), phenylacetyl chloride (TCI, 98%), aluminium chloride (Wako, 99%), $KHCO_3$ (Wako, 99.5%), K_2CO_3 (Wako, 99.5%), 6–8 kD MWCO SpectraPor standard RC dry dialysis membrane.

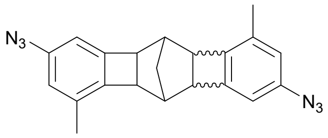
Synthesis of S1.



S1

The compound **S1** was synthesized according to a modified procedure reported in the literature[1]. Thus, into a pressure-resistant schlenk flask, 4-bromo-3-methylaniline (8.00 g, 43.9 mmol), norbornadiene (2.24 mL, 22.0 mmol), $Pd(OAc)_2$ (1 mol%), PPh_3 (2 mol%), Cs_2CO_3 (14.3 g, 4.39 mmol), and dioxane (40 mL) were added. Then the mixture was stirred at 150ºC for 6 h. After cooled to room temperature, the mixture was filtered through celite and concentrated. The obtained solid was recrystallized in cold MeOH to afford **S1** as a brown powder (4.27 g, 66%). ^1H NMR (500 MHz, $CDCl_3$) δ ppm 6.33 (s, 2H), 6.22 (s, 2H), 3.49 (br s, 4H), 3.11 (4H), 2.09 (2H), 0.79 (s, 2H).

Synthesis of 1.



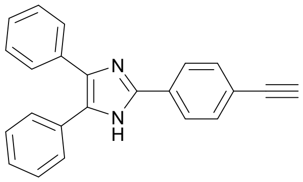
1

Into a two-neck flask, **S1** (1.24 g, 4.1 mmol), ADMP (2.69 g, 9.4 mmol), DMAP (1.10 g, 9.0 mmol), and CH_2Cl_2 (30 mL) was added, and stirred at room temperature. After 1 h, aqueous $NaHCO_3$ solution (30 mL) was added to quench to reaction. Then the mixture was separated in CH_2Cl_2 and H_2O. The organic layer was washed sequentially with aqueous HCl solution and H_2O, dried over anhydrous magnesium sulfate and evaporated to dryness. The crude solid was purified by silica gel column chromatography (silica gel, hexane/ethyl acetate = 9:1), to afford **1** as a brown powder (1.02 g, 70%). ^1H NMR (500 MHz, $CDCl_3$) δ ppm 6.64 (s, 2H), 6.56 (s, 2H), 3.22 (4H), 2.37 (2H), 2.17 (s, 6H), 0.75 (s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm 147.95, 146.90, 141.52, 139.74, 134.01, 133.96, 119.24, 119.22, 110.37, 48.23, 47.84, 36.82, 26.29, 16.69.

Synthesis of S2.

The compound **S2** was synthesized according to the reported procedure[2].

Synthesis of 2a.



2a

Into a 30 mL flask, **S2** (0.65 g, 5.0 mmol), benzil (1.05 g, 5.0 mmol), ammonium acetate and MeOH (5 mL) were added. The mixture was refluxed at 75 ºC overnight. After cooling to room temperature, the precipitate was collected by filtration washing with MeOH, and then dried under reduced pressure to afford **2a** as a yellow powder (1.14 g, 71%). ^{1}H NMR (500 MHz, acetone-d_6) δ ppm 11.85 (s, 1H), 8.14 (d, 2H), 7.68-7.24 (12H), 3.76 (s, 1H).

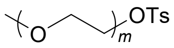
Synthesis of S3.

The compound **S3** was synthesized according to the reported procedure[3].

Synthesis of 2b.

The compound **2b** was synthesized according to the reported procedure[4].

Synthesis of S4.



S4

In a 100 mL 2-neck flask, Poly(ethylene glycol) methyl ether (M_n~2000) (5 g) was dissolved in THF (12 mL), and then NaOH (1 g, 25 mmol) in H_2O (2.5 mL) was added. The mixture was cooled to 0 ºC, and then TsCl (0.95 g, 5 mmol) dissolved in THF (10 mL) was added dropwise to the reaction mixture. The reaction mixture was stirred for 16 h at room temperature. At this point, H_2O (20 mL) was added and stirred for extra 30 min. CH_2Cl_2 was added to extract the product and concentrated. The concentrated solution was added dropwise into excess amount of cold Et_2O. The generated precipitate was collected and dried in vacuum at 80 ºC to afford **S4** as a white solid (4.67 g, 85%). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 7.80 (d, 2H), 7.50 (d, 2H), 4.12 (t, 2H), 3.52 (m), 3.25 (s, 3H), 2.43 (s, 3H).

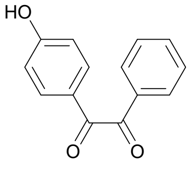
Synthesis of S5.

The compound **S5** was synthesized according to the reported procedure[5].

Synthesis of S6.

The compound **S6** was synthesized according to the reported procedure[6].

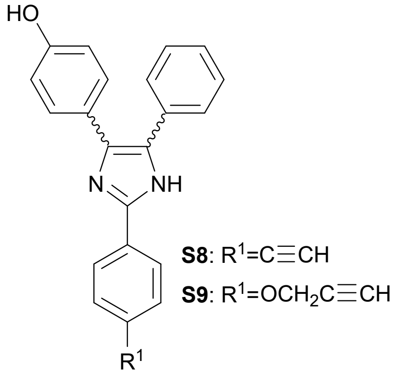
Synthesis of S7.



S7

Into a 50 mL flask, **S6** (3.85 g, 16 mmol), CH_3COOH (20 mL) and HBr (20 mL) were added and refluxed at 150 ºC for 14 h. After cooled to r.t., the mixture was poured into H_2O (300 mL), then the precipitate was collected by filtration. The crude product was dissolved in aqueous NaOH solution (20 mL, pH = 14), and then aqueous HCl solution (1 M) was added dropwise until pH became 7. Precipitates formed were collected by filtration and washing with H_2O, affording **S7** as a reddish brown powder (2.46 g, 68%). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 10.92 (1 H, s), 7.91 (2 H, d), 7.78 (3 H, m), 7.63 (2 H, t), 6.94 (2 H, d).

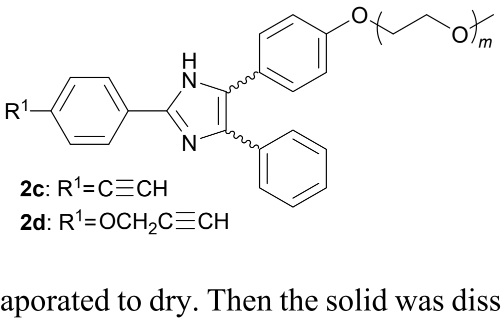
Synthesis of S8 and S9.



Into a 50 mL 2-neck flask, **S7** (1.0 g, 4.4 mmol), **S2** (0.60 g, 4.6 mmol), CH_3COONH_4 (1.36 g, 17.6 mmol) and MeOH (10 mL) were added. The mixture was refluxed at 85ºC for 14 h. Then the mixture was cooled to −20ºC. The generated precipitate was collected by filtration washing with cold MeOH, and then dried in vacuum, affording **S8** as a yellow powder (1.05 g, 65%). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 12.68 (s, 1H), 9.71, 9.41 (s, 1H), 8.09 (d, 2H), 7.58–7.21 (m, 9H), 6.84, 6.71 (d, 2H), 4.30 (s, 1H). HR-MS (ESI$^+$) calculated for $C_{23}H_{16}N_2O$, $[M+H]^+$ 337.1335, found 337.1348 (error 4 ppm).

Likewise, **S9** was synthesized with **S7** (1.0 g, 4.4 mmol), **S3** (0.75 g, 4.6 mmol), and CH_3COONH_4 (1.36 g, 17.6 mmol) and obtained as a yellowish pink powder (1.05 g, 65%). ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 12.40 (m, 1H), 9.66, 9.37 (s, 1H), 8.01 (d, 2H), 7.57-7.18 (m, 7H), 7.10 (d, 2H), 6.84, 6.71 (d, 2H), 4.86 (d, 2H), 3.62 (t, 1H). HR-MS (ESI$^+$) calculated for $C_{24}H_{18}N_2O_2$, $[M+H]^+$ 367.1441, found 367.1457(error 4 ppm).

Synthesis of 2c and 2d.



Into a 20 mL vial, **S4** (1.0 g), **S8** (612 mg, 4 eq.), K_2CO_3 (25 mg, 4eq.) and anhydrous CH_3CN (10 mL) was added and stirred at 75ºC for 2 h. Then the solution was cooled to room temperature, evaporated to dry and dissolved in CH_2Cl_2, dried over $MgSO_4$ and evaporated to dry. Then the solid was dissolved in EtOH at room temperature, and cooled to −20ºC. The formed crystal was collected by filtration washing with cold EtOH and Et_2O respectively, and then dried in vacuum to afford **2c** as a yellow powder (600 mg, 56%). ^1H NMR (500 MHz, acetone-d_6) δ ppm 8.16 (d, 2H), 7.67 (d, 2H), 7.61 (d, 2H), 7.56 (d, 2H), 7.39 (t, 2H), 7.31 (t, 1H) 6.99 (d, 2H), 4.21 (t, 2H), 3.86 (t, 2H), 3.77 (s, 1H), 3.60 (m), 3.32 (s, 3H). Number averaged molecular weight (M_n), weight averaged molecular weight (M_w), peak molecular weight (M_p), and dispersity ($Đ = M_w/M_n$) measured by size exclusion chromatography (SEC) calibrated with poly(ethylene oxide) standards; $M_n = 2100$, $M_w = 2300$, $M_p = 2200$, $Đ = 1.06$.

Likewise, **2d** was synthesized from **S4** and **S9**. The product was afforded as a yellowish white powder (530 mg, 49%). ^1H NMR (500 MHz, acetone-d_6) δ ppm 8.08 (d, 2H), 7.70-7.20 (m, 7H), 7.20 (d, 2H), 7.03-6.93 (2H), 4.88 (d, 2H), 4.22–4.17 (m, 2H), 3.89 (m, 2H), 3.58 (m), 3.31 (s, 3H), 3.15(t, 1H) (Figure S9). The M_n, M_w, M_p, and $Đ$ measured by SEC calibrated with PEO standards; $M_n = 2100$, $M_w = 2200$, $M_p = 2200$, $Đ = 1.04$.

Synthesis of L1 and L2.

Into a vial, **1**(120 mg, 0.34 mmol) and **2a** (228 mg, 0.71 mmol), CuBr (97 mg, 0.68 mmol), PMEDTA (141 μL, 0.68 mmol) and THF (2 mL) were added, and then stirred for 4 h. The mixture was poured into MeOH. The precipitate was collected by filtration washing with MeOH and then dried under reduced pressure. **L1** was afforded as a light yellow powder (266 mg, 79%). ^1H NMR (500 MHz, DMSO-d_6) δ ppm 12.75 (s), 9.29 (d, 2H), 8.22 (d, 4H), 8.04 (d, 4H), 7.65–7.24 (24H), 2.33 (6H, t), 0.78 (s, 2H). HR-MS (ESI$^+$) calculated for $C_{67}H_{50}N_{10}$, $[M+H]^+$ 995.4293, found 995.4305 (error 1.2 ppm).

Likewise, **L2** was synthesized from **1** and **2b**, the product was a light yellow powder (88%). ^1H NMR (500 MHz, DMSO-d_6) δ ppm 12.54 (2H, s), 8.88 (d, 2H), 8.05 (d, 4H), 7.85–7.20 (28H), 5.30 (s, 4H), 2.31 (d, 7H), 0.74 (s, 2H). HR-MS (ESI$^+$) calculated for $C_{69}H_{54}N_{10}O_2$, $[M+H]^+$ 1055.4504, found 1055.4518 (error 1.3 ppm).

Synthesis of H1 and H2.

Into a flask, **L1** (75 mg) and 75 mL CH_2Cl_2 were added. Then aqueous solution (5 mL) of $K_3[Fe(CN)_6]$ (376 mg, 1 mmol) and KOH (56 mg, 1 mmol) was added in dark. The mixture was stirred at room temperature for 4 h. After reaction, the organic layer was washed by H_2O and dried over anhydrous magnesium sulfate. The solution was concentrated and passed through a plug of alumina in Pasteur pipet. Finally, the solution was evaporated to give the product as a yellow powder (59 mg, 79%). ^1H NMR (500 MHz, CD_2Cl_2) δ ppm 8.46–6.05 (34H), 3.31 (4H), 2.44 (2H), 2.25 (6H), 0.80 (2H). HR-MS (ESI$^+$) (Sciex5600) calculated for $(C_{67}H_{48}N_{10})_2$, $[M+2H]^{2+}$ 993.4142, found 993.4104 (error 3.8 ppm).

Likewise, **H2** was synthesized from **L2** (concentration: 1 mg/mL). The product was afforded as a green powder (72%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 8.43–6.61 (34H), 5.14 (4H), 3.37 (4H), 2.52 (2H), 2.30 (6H), 0.84 (2H). MS (ESI$^+$) (T100LC) calculated for $(C_{69}H_{52}N_{10}O_2)_2$, $[M+2H]^{2+}$ 1053.435, found 1053.678.

Synthesis of L3 and L4.

Into a 4 mL vial, **1** (15.3 mg), **2c** (200 mg), CuBr (12.4 mg), PMEDTA (15 mg), and THF (1 mL) were added. The mixture was stirred at room temperature for 4 h. After reaction, the mixture was passed through a plug of alumina using $CHCl_3$ as an eluent. The eluent was collected and evaporated to dry to give a crude product as yellow solid. Then the obtained solid was dissolved in MeOH and loaded into a dialysis tube. The dialysis tube was placed into an excess amount of MeOH and stirred for 12 h. Then the dialysis tube was placed into another fresh MeOH and stirred for another 24 h. External MeOH of the second dialysis was collected and evaporated to dryness. The obtained solid was dissolved in EtOH at room temperature. The EtOH solution was cooled to −20 ºC, and the formed precipitate was collected by filtration, washing with cold EtOH and Et_2O respectively, and then dried under reduced pressure to afford **L3** as a yellow powder (75 mg, 35%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 10.54, 10.35 (s), 8.32 (d, 2H), 8.16 (d, 4H), 8.04 (d, 4H), 7.72-7.21 (18 H), 7.02, 6.93 (d, 4H), 4.23, 4.18 (t, 4H), 3.89 (4H), 3.63 ($–OCH_2CH_2O–$), 3.37 (s, 6H), 2.61 (2H), 2.39 (6H), 0.94 (s, 2H). The M_n, M_w, M_p, and $Đ$ measured by SEC calibrated with PEO standards; $M_n = 4900$, $M_w = 5200$, $M_p = 5100$, $Đ = 1.05$.

Likewise, **L4** was synthesized and isolated by dialysis. The product was afforded as a light brown powder (34 mg, 16%). ^{1}H NMR (500 MHz, acetone-d_6) δ ppm 11.68 (s), 8.62 (d, 2H), 8.13 (d, 4H), 7.72-7.21 (22H), 7.01, 6.90 (4H), 5.35 (s, 2H), 4.19 (4H), 3.84 (4H), 3.59 ($–OCH_2CH_2O–$), 3.30 (s, 6H), 2.57 (2H), 2.34 (6H), 0.84 (s, 2H). The M_n, M_w, M_p, and $Đ$ measured by SEC calibrated with PEO standards; $M_n = 4900$, $M_w = 5100$, $M_p = 5100$, $Đ = 1.05$.

Synthesis of H3 and H4.

Into a 20 mL vial, **L3** (20 mg) and CH_2Cl_2 (4 mL) were added. Then aqueous solution (1 mL) of $K_3[Fe(CN)_6]$ (82 mg, 0.25 mmol) and KOH (14 mg, 0.25 mmol) was added in dark. The mixture was stirred at room temperature for 2 h, and then extracted by CH_2Cl_2. The extract was washed by H_2O and dried over anhydrous magnesium sulfate. Then the solution was evaporated to dryness to afford **H3** as a yellow solid (78%). ^{1}H NMR (500

MHz, CD_2Cl_2) δ ppm 8.22–6.61 (16H), 4.17-3.95, 3.52 ($–OCH_2CH_2O–$), 3.25 (s, 3H), 2.49, 2.25 (4H), 0.80 (1H).

Similarly, **H4** was synthesized from **L4** and was afforded as a light green solid (72%). ^1H NMR (500 MHz, CD_2Cl_2) δ ppm 8.30–6.50 (16H), 3.54 ($–OCH_2CH_2O–$), 3.26 (s, 3H), 2.45(1H), 2.22 (3H), 0.76 (1H).

Scission and reformation of polymers upon photoirradiation.

Photoirradiation experiments were conducted using a compact Xenon Light source MAX-350 (Asahi spectra). **H1** and **H2** were dissolved in THF (without stabilizer) and prepared polymer solution at the concentration of 5, 10, 50, 80, 100 mg/mL, respectively. Each solution was irradiated by UV (λ = 365 nm, 70 mW/cm^2) for 2 min. The solutions were kept in the dark for 12 h before SEC measurements.

NMR measurements.

^1H NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 500 MHz. $CDCl_3$, CD_2Cl_2, DMSO-d_6, acetone-d_6 were used as the solvent and chemical shifts were reported relative to tetramethylsilane (TMS) (δ = 0.00 ppm) or solvent residual signals.

SEC measurements.

SEC measurements were conducted using a Waters e-2695 high-speed liquid chromatograph equipped with refractive index (RI) and UV detectors at 40 °C. A KF-603 (Shodex) was employed with tetrahydrofuran (THF) as the eluent at a flow rate of 0.5 mL/min.

UV- vis absorbance measurements.

UV-vis absorption spectra were recorded on a SHIMADZU UV-1900i spectrometer. For time-course measurements upon ON–OFF cycles of photoirradiation, absorbance at the wavelength of 600 nm (A_{600}) was plotted against time.

Self-assembly.

A weighed amount of **L3** (1 mg) was dissolved in THF and H_2O (1 mL) water was slowly added into the solution until the solution became slightly turbid. The remaining THF was evaporated and then H_2O was added until the total volume of dispersion became 1 mL. Likewise, self-assembly of **L4**, **H3** and **H4** was performed.

Transmission electron microscopy (TEM) observation.

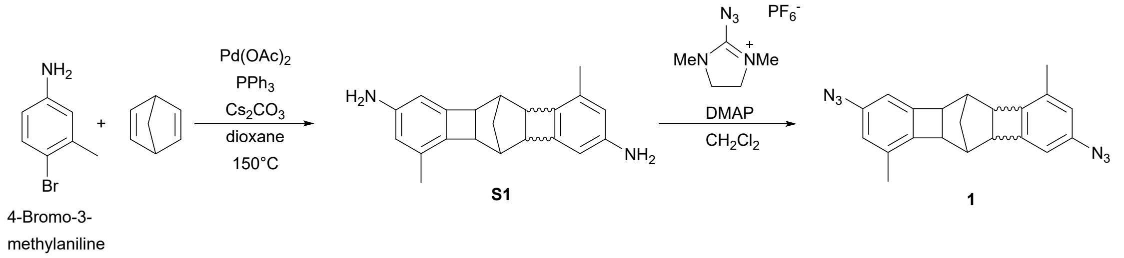
A formvar/carbon coated Cu grid (200 mesh) was plasma glow discharged for 15 s to hydrophilize the surface. An aqueous suspension (10 μL) of a specimen was placed on the surface of the grid for 30 s, and the excess suspension was removed using a filter paper. For photoirradiated sample, the suspension was irradiated with UV (λ = 365 nm) for a few minutes before removing the excess suspension with a filter paper. The sample-loaded grids were carefully dried under air. TEM observations were performed on a Hitachi H-7600 operating at 80 kV accelerating voltage.

Molecular modeling and calculations.

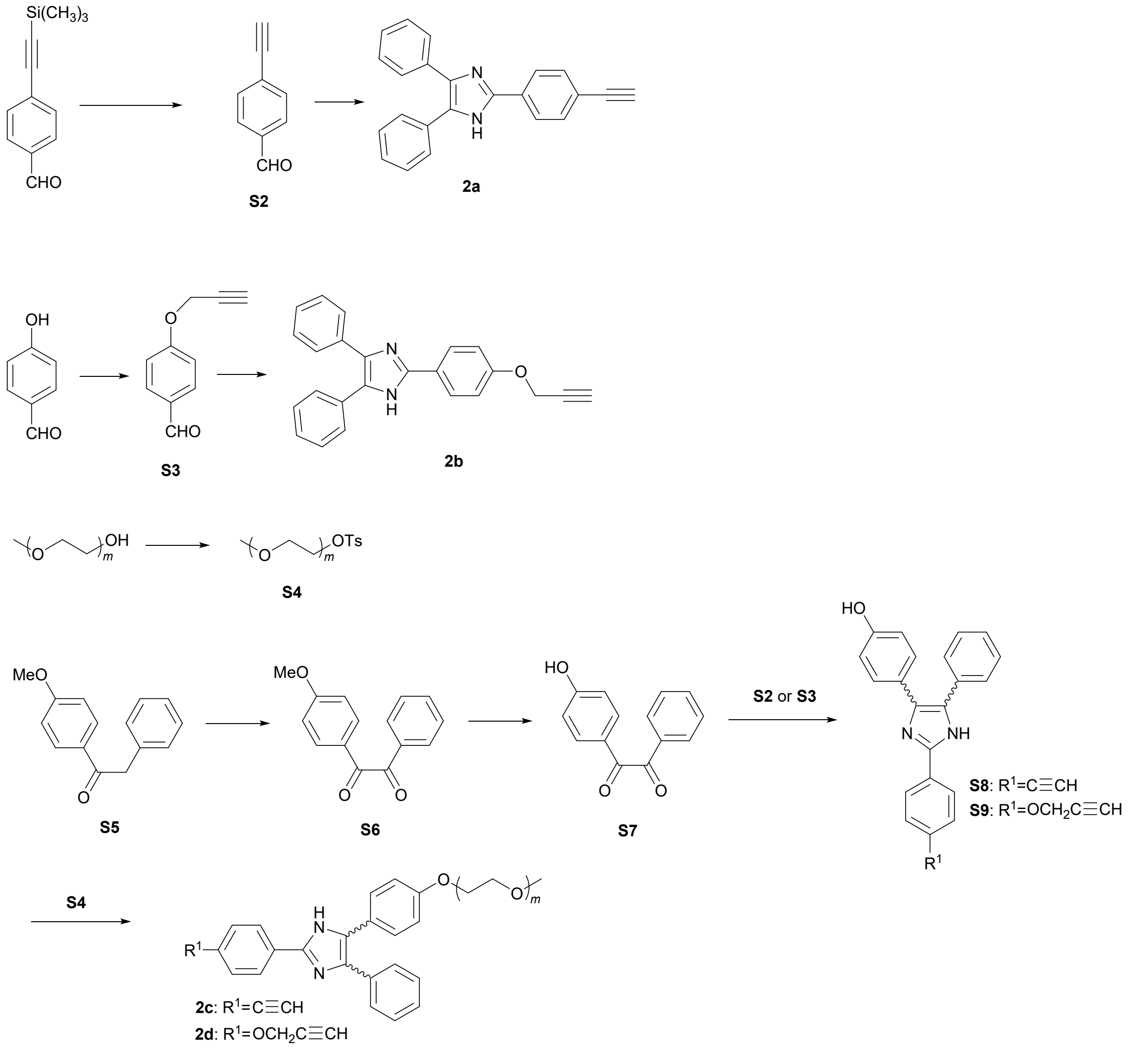
Molecular modeling and molecular mechanics (MM2) calculation was carried out using a PerkinElmer Chem3D 19.1 software. The energy minimization was conducted with a minimum RMS gradient of 0.01.

Light scattering measurements.

Dynamic light scattering (DLS) measurements were performed on a Wyatt DynaPro plate reader with a 96-well glass plate. Averaged hydrodynamic diameters (D_hs), D_h distributions, and polydispersity indices (PdI) of nanoparticles were calculated with a Dynamics 7.1 software built into the instrument



Scheme S1 Synthetic route of **1**



Scheme S2 Synthetic route of **2a**, **2b**, **2c**, and **2d**.

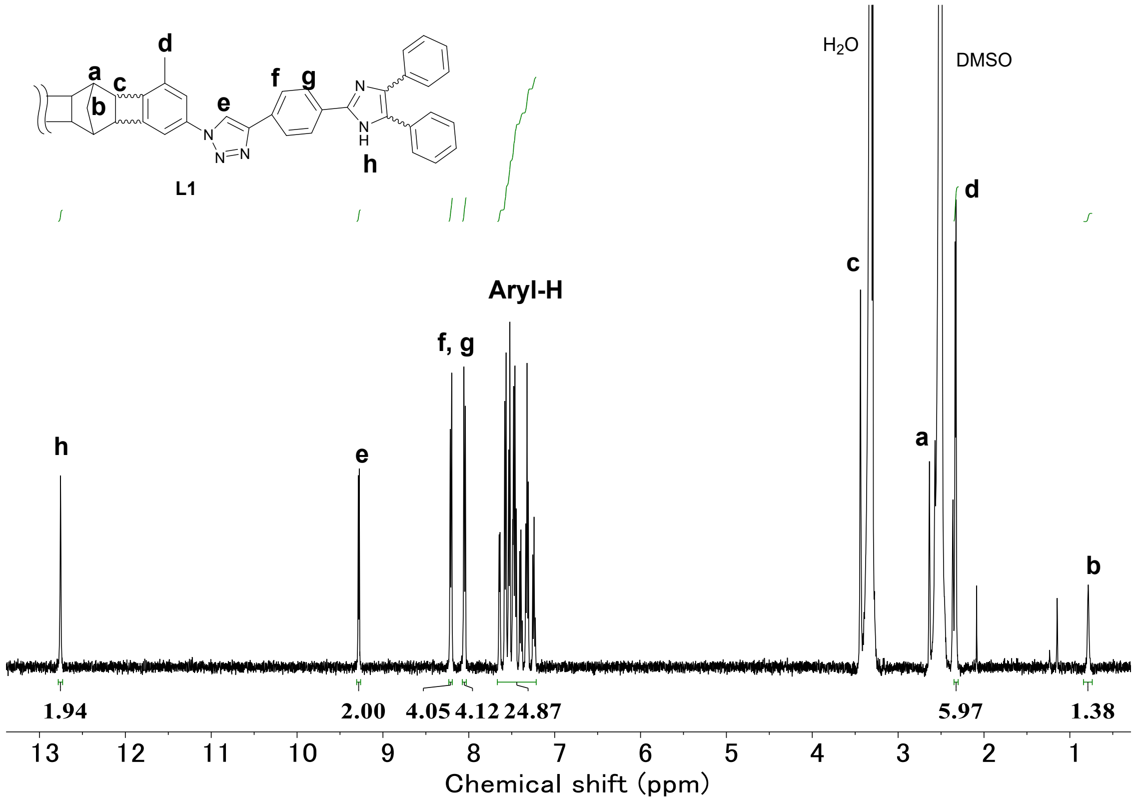


Figure S1. ^{1}H NMR spectrum of **L1** (DMSO-d_6, 25 °C).

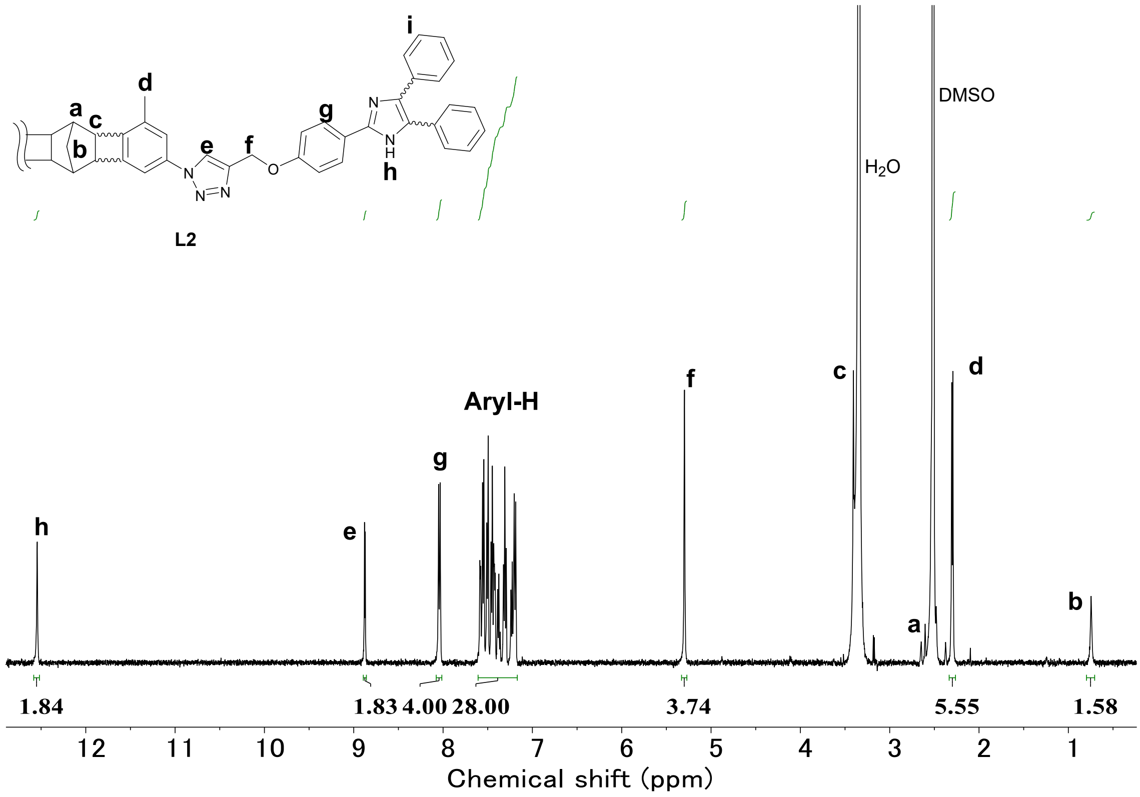


Figure S2. ^{1}H NMR spectrum of **L2** (DMSO-d_6, 25 °C).

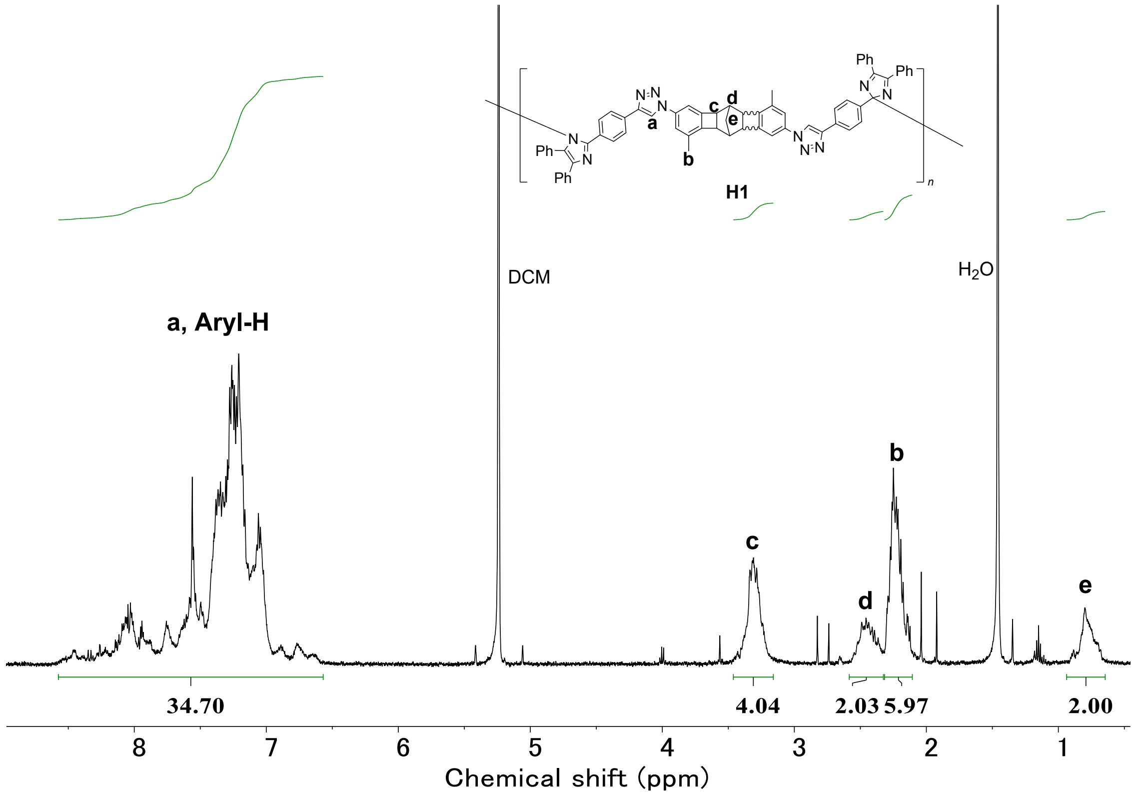


Figure S3. ^{1}H NMR spectrum of **H1** (CD_2Cl_2, 25 °C)

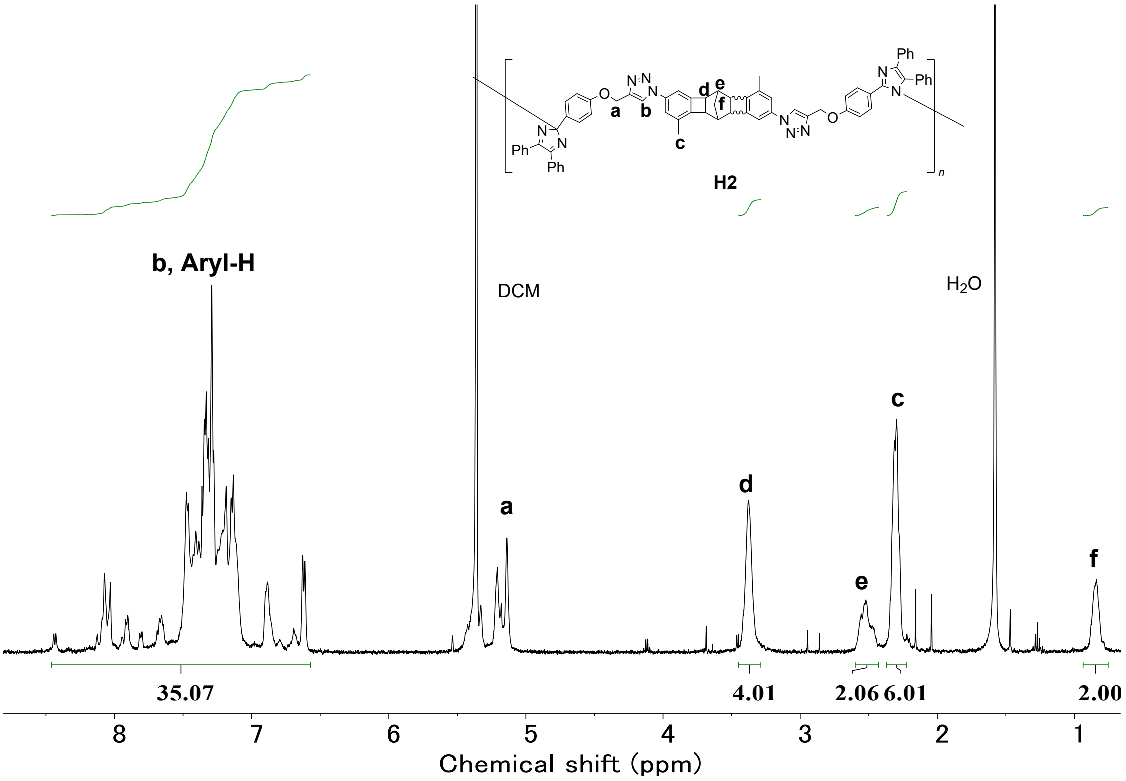


Figure S4. ^{1}H NMR spectrum of **H2** (CD_2Cl_2, 25 °C)

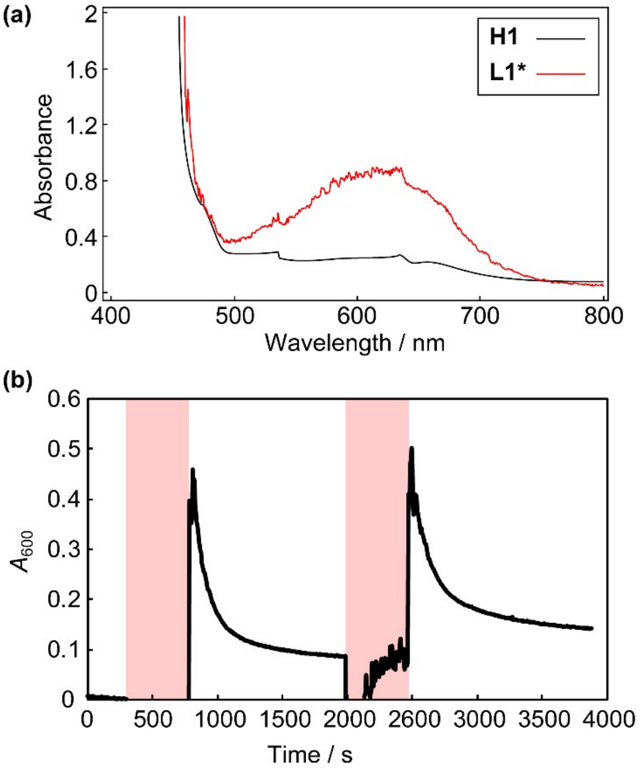


Figure S5. (a) UV-vis spectra of **H1** (black line) and **L1*** (red line). The spectrum of **L1*** was recorded immediately after photoirradiation ($\lambda = 365$ nm). (b) Time-dependent plots of A_{600} upon ON–OFF cycles of photoirradiation ($\lambda = 365$ nm). The sample was irradiated during time ranges indicated in pink.

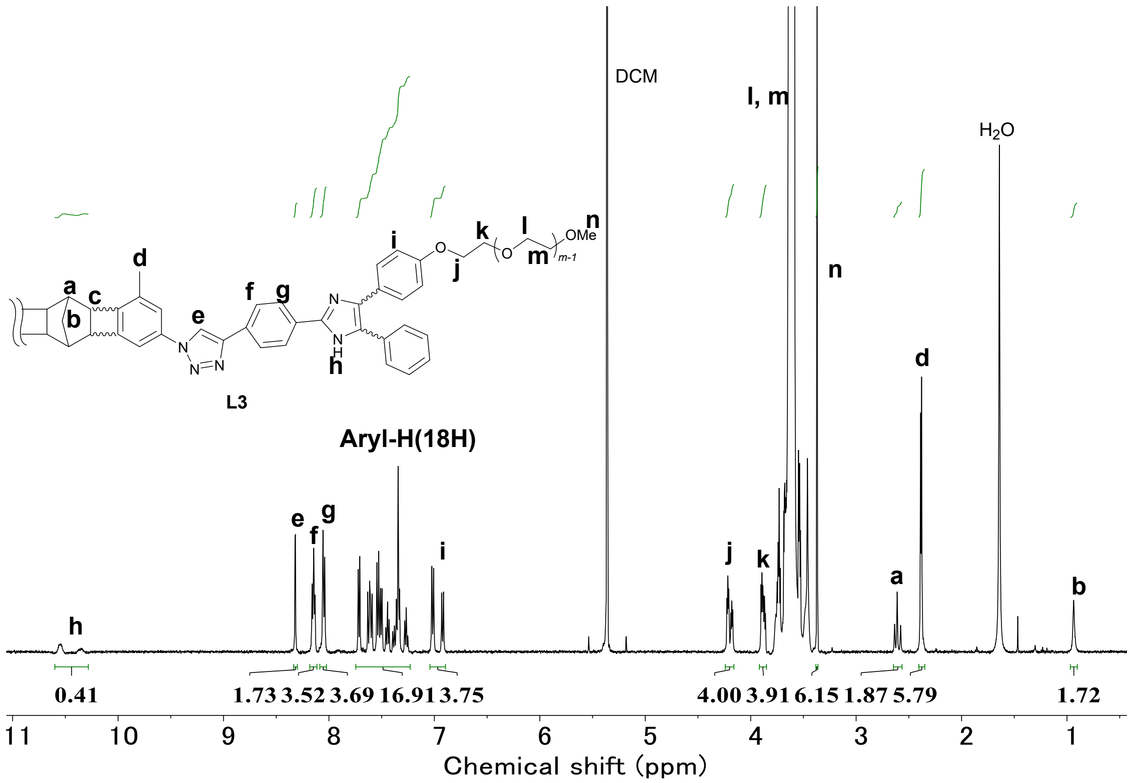


Figure S6. ^{1}H NMR spectrum of **L3** (CD_2Cl_2, 25 °C)

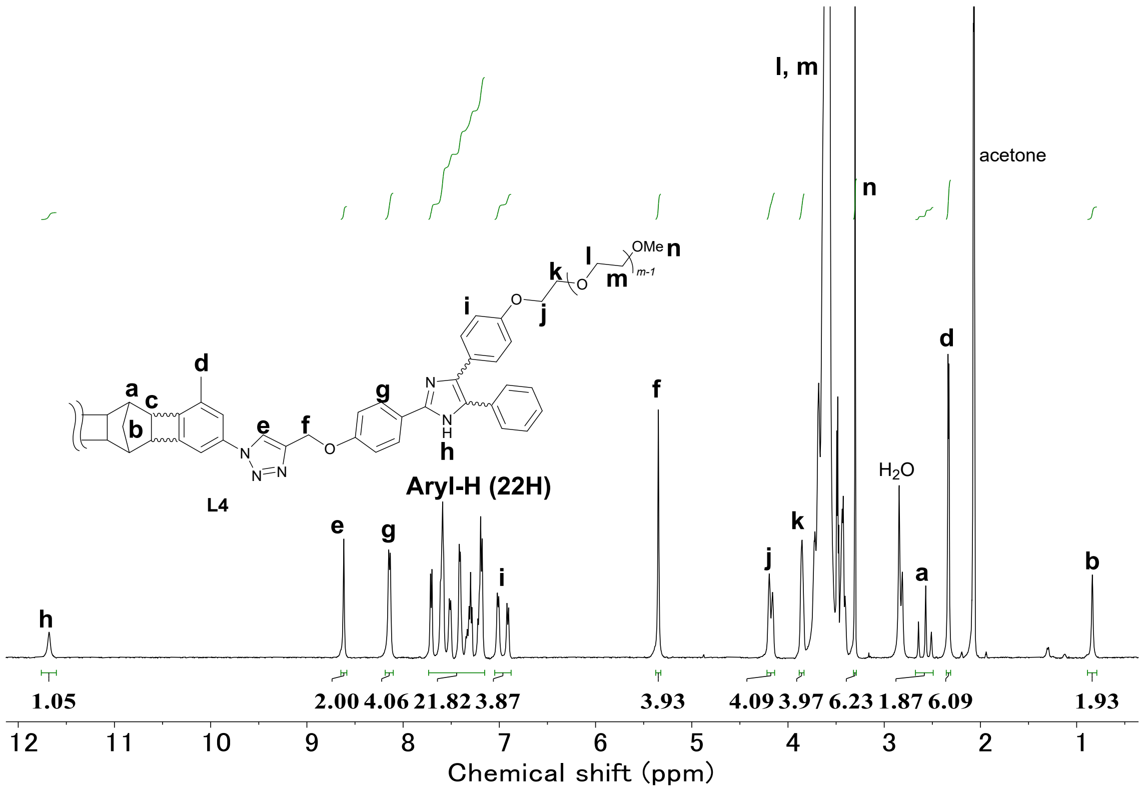


Figure S7. ^{1}H NMR spectrum of **L4** (acetone, 25 °C)

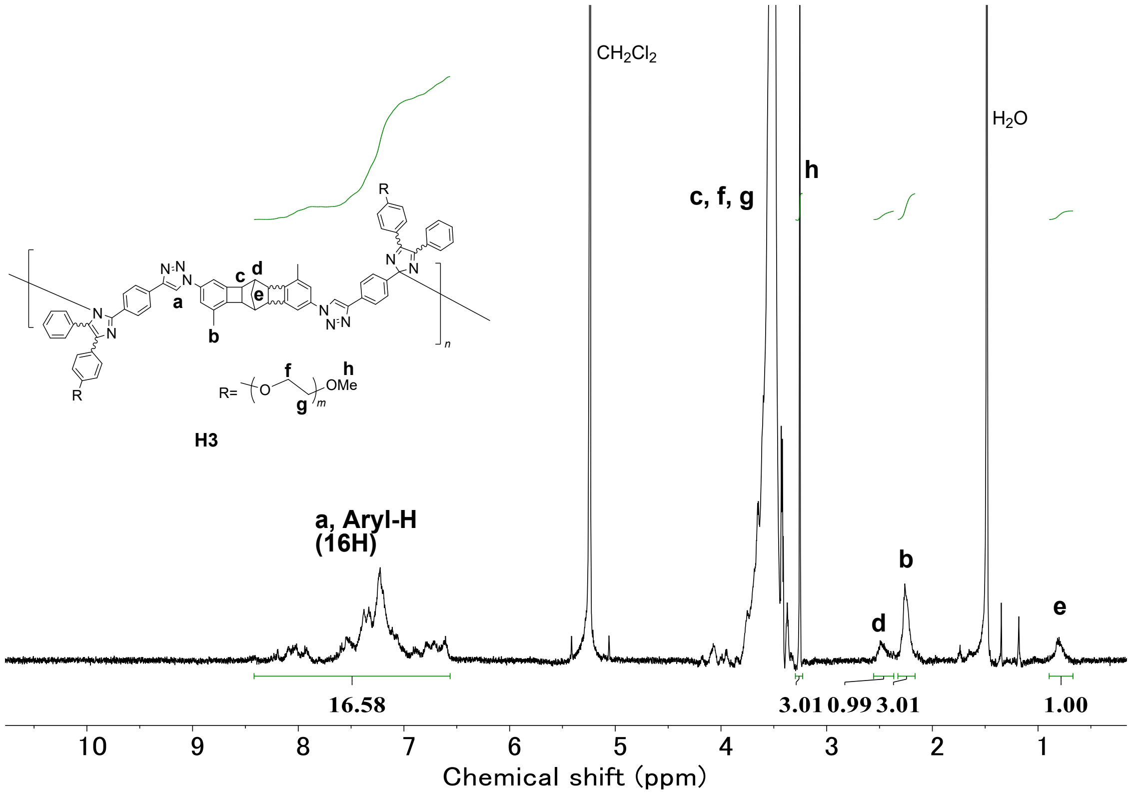


Figure S8. ^{1}H NMR spectrum of **H3** (CD_2Cl_2, 25 °C)

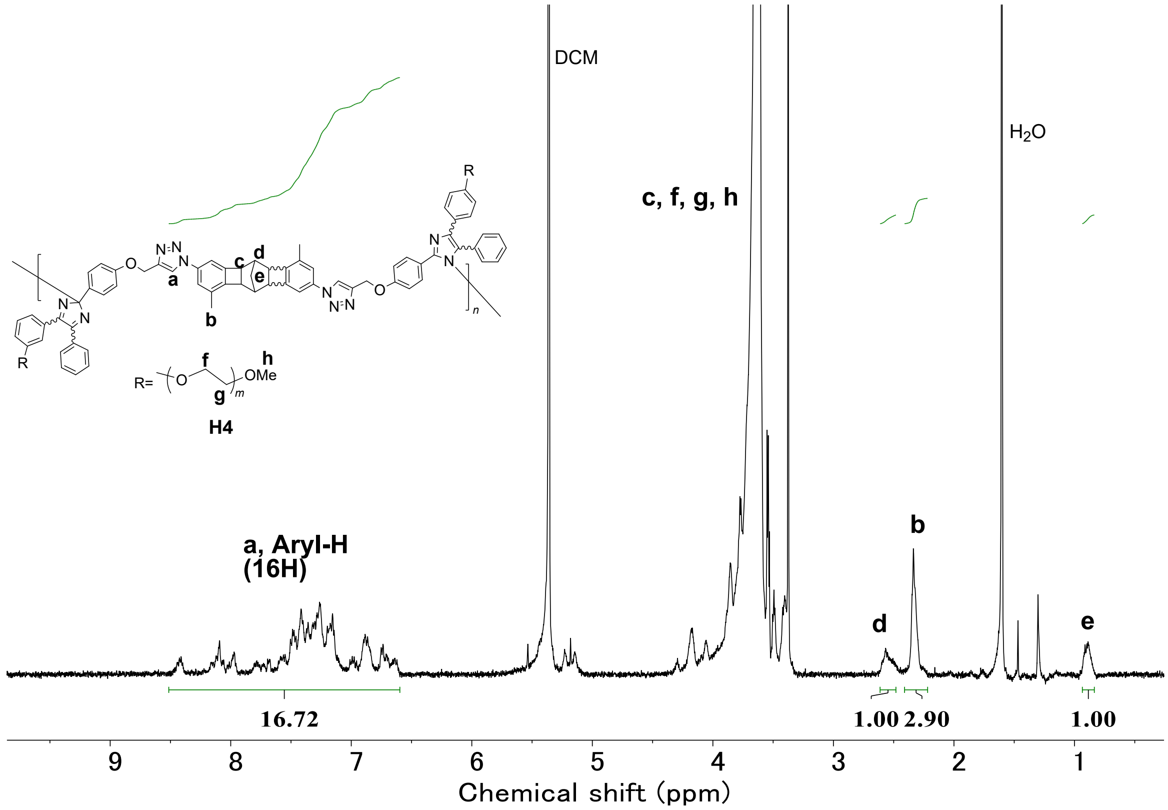


Figure S9. ^{1}H NMR spectrum of **H4** (CD_2Cl_2, 25 °C)

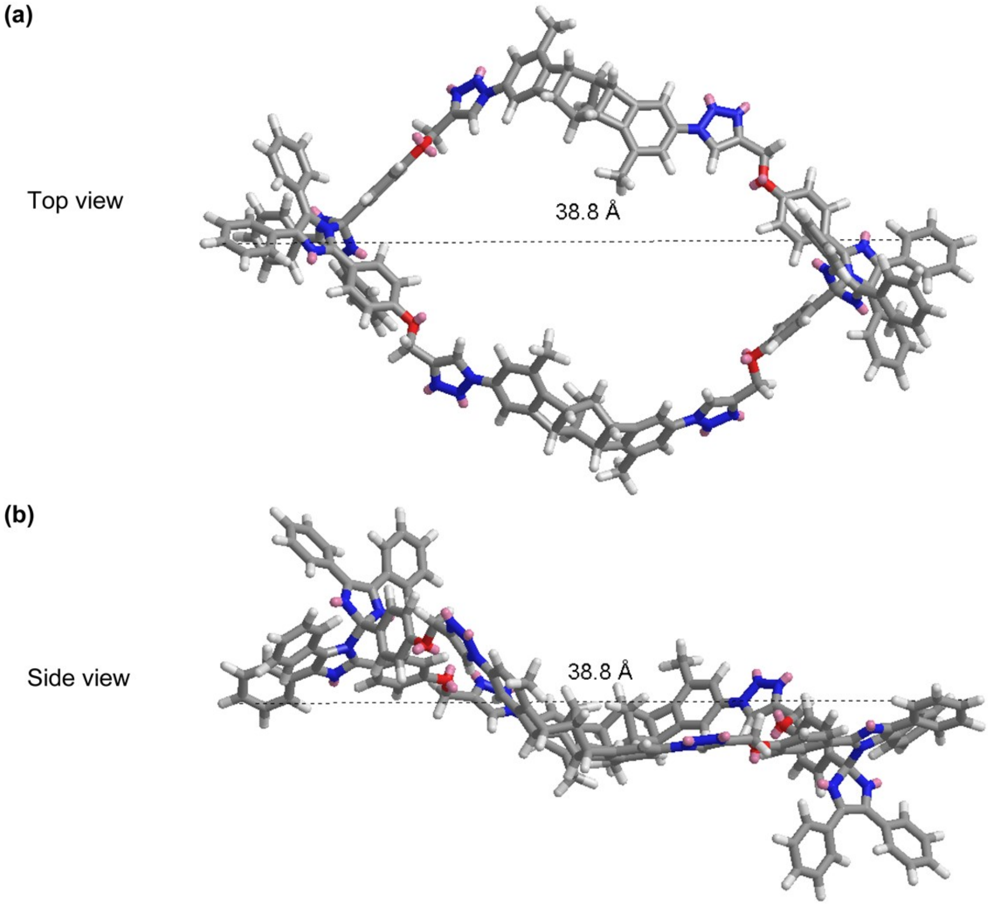


Figure S10. MM2-calculated structure of $\mathbf{H4}_{(2)}$; (a) top view and (b) side view.

References

1. M. A. Abdulhamid, H. W. H. Lai, Y. G. Wang, Z. X. Jin, Y. C. Teo, X. H. Ma, I. Pinnau and Y. Xia, *Chem. Mater.*, 2019, **31**, 1767-1774.
2. W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280-2286.
3. C. Liu, W. Ding, Y. Liu, H. Zhao and X. Cheng, *New J. Chem.*, 2020, **44**, 102-109.
4. S. Honda and T. Toyota, *Nat. Commun.*, 2017, **8**, 502.
5. D. Ganapathy and G. Sekar, *Org. Lett.*, 2014, **16**, 3856-3859.
6. R. Chebolu, A. Bahuguna, R. Sharma, V. K. Mishra and P. C. Ravikumar, *Chem. Commun.*, 2015, **51**, 15438-15441.