

Supporting Information

Photolysis of Polymeric Self-Assembly Controlled by Donor- Acceptor Interaction

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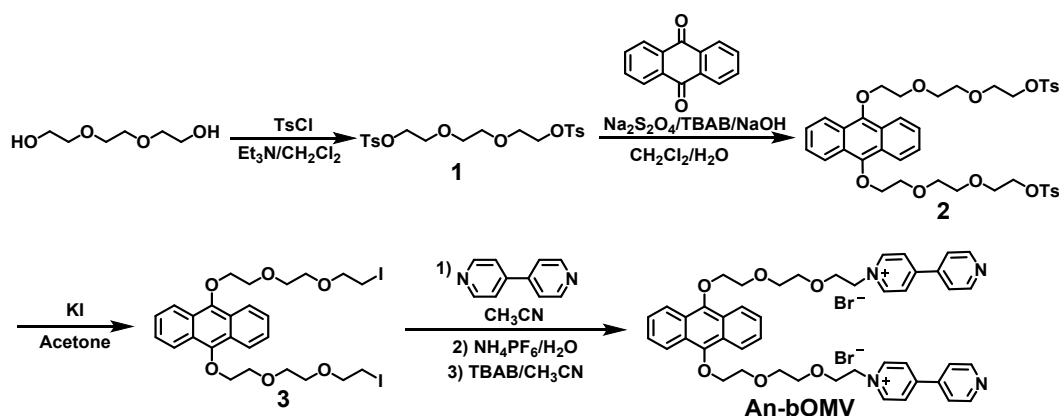
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1. General information

The commercially available reagents and solvents were used as purchased. All yields were given as isolated yields. The pre-irradiated solution, which was bubbled for 30 min by oxygen, was placed in centrifugal tubes (5 mL) and further irradiated using a 300 W Xenon lamp (CEL-HXF300). The regulation of pH is executed by hydrochloric acid and sodium hydroxide. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^1H - ^1H NOESY spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 at 25 °C. ^1H NMR spectra recorded in D_2O were referenced to the internal CH_3CN signal at 2.06 ppm. MALDI-TOF mass spectra were recorded on a Bruker New Autoflex Speed LIN Spectrometer using a 337 nm nitrogen laser with dithranol as matrix. UV-vis absorption spectra were obtained on a PerkinElmer Lambda 750 spectrophotometer at 25 °C. Fluorescence spectra were recorded on a Hitachi model F-7000 spectrofluorometer. Atomic force microscopy (AFM) was performed on a Bruker Multimode 8 on the mica sheet. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on a Bruker mior OTOF-QII spectrometer. The Electrospray Ionization Mass Spectra (EI-MS) were recorded on a SHIMADZU GCMS-QP2010 SE. The cyclic voltammetry experiments were carried out on a CHI660E B14511 electrochemical workstation comprising a platinum carbon working electrode, a Pt coil counter electrode, and a $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (SCE) reference electrode. The hydrodynamic diameter (D_h) was determined by DLS experiments at 25 °C. Solution samples were examined by NanoBrook 173 plus at scattering angle of 90°. Viscometer measurements were carried out on a SCHOTT-Ubbelohde micro capillary viscometer (DIN 53810, 0.40 mm inner diameter) at 30 °C.

2. Synthesis of An-bOMV



Scheme S1. Synthesis of An-bOMV.

Synthesis of Compound 1.¹ A mixture of triethylene glycol (8.0 mL, 0.06 mol), Et₃N (25.0 mL, 0.18 mol) was dissolved in CH₂Cl₂ (100 mL). A solution of tosyl chloride (25.0 g, 0.13 mol) in CH₂Cl₂ (40 mL) was added in portions to this mixture during 1 h under a nitrogen atmosphere. After that, the reaction mixture was stirred overnight at room temperature. It was then washed with saturated NaHCO₃ aqueous solution. The organic phase was dried by MgSO₄ and the solvent was removed via rotary evaporation under reduced pressure. The crude product was purified by column chromatography over silica gel with CH₂Cl₂/petroleum ether to afford **1** as a white solid (19.4 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.0 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 4H), 4.08–4.06 (m, 4H), 3.60–3.57 (m, 4H), 3.46 (s, 4H), 2.38 (s, 6H).

Synthesis of Compound 2.² A mixture of compound **1** (13.0 g, 28.5 mmol), 9,10-anthraquinone (1.0 g, 4.8 mmol), and tetrabutylammonium bromide (TBAB) (1.6 g, 4.8 mmol) was dissolved in CH₂Cl₂ (50 mL) under a nitrogen atmosphere. Then the solution of Na₂S₂O₄ (1.7 g, 9.5 mmol) and NaOH (1.9 g, 47.7 mmol) in nitrogen-saturated water (50 mL) was added in portions, and the mixture was stirred under reflux at 40 °C for 5 days. After cooling to room temperature, it was then washed with saturated NaCl aqueous solution, and the organic phase was dried by MgSO₄. The solvent was removed via rotary evaporation under reduced pressure, and the resulting residue was purified by column chromatography with CH₂Cl₂/petroleum ether to yield

2 (0.7 g, 19%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.27 (dd, $J = 6.4$ Hz, 2.8 Hz, 4H), 7.71 (d, $J = 8.0$ Hz, 4H), 7.39 (dd, $J = 6.8$, 3.2 Hz, 4H), 7.20 (d, $J = 8.4$ Hz, 4H), 4.29–4.21 (m, 4H), 4.17–4.09 (m, 4H), 3.94–3.85 (m, 4H), 3.72–3.69 (m, 8H), 3.67–3.66 (m, 4H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.03, 143.76, 131.91, 128.77, 126.93, 124.31, 124.06, 121.65, 73.75, 69.91, 69.62, 68.28, 67.86, 20.25. MALDI-TOF: m/z 782.243 ($[\text{M}]^+$, calcd for $\text{C}_{40}\text{H}_{46}\text{O}_{12}\text{S}_2^+$, 782.243).

Synthesis of Compound 3.³ A mixture of compound **2** (0.65 g, 0.83 mmol) and KI (1.4 g, 8.3 mmol) in acetone (60 mL) was heated under reflux in a nitrogen atmosphere for 24 h and evaporated to dryness after cooling. The residue was washed with CH_2Cl_2 and saturated $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution. The organic phase was dried by MgSO_4 . The solvent was removed via rotary evaporation under reduced pressure, and the resulting residue was purified by column chromatography with EtOAc/petroleum to yield **3** as a white solid (250 mg, 43%). ^1H NMR (400 MHz, CDCl_3): δ 8.30 (dd, $J = 6.8$, 3.2 Hz, 4H), 7.41 (dd, $J = 6.8$, 3.2 Hz, 4H), 4.44–4.21 (m, 4H), 4.03–3.88 (m, 4H), 3.88–3.62 (m, 12H), 3.23 (t, $J = 13.6$ Hz, 4H).

Synthesis of Compound An-bOMV.³ A solution of 4,4-bipyridine (2.25 g, 14.4 mmol) in CH_3CN (40 mL) was refluxed under a nitrogen atmosphere. Compound **3** (1.0 g, 1.4 mmol) was added in portions during 3 days, seven times per day (40 mg per portion). The reaction mixture was maintained under reflux for further 48 h, and then was cooled at 4 °C overnight. The precipitate was collected and dissolved in a minimum of water, followed by the addition of excess NH_4PF_6 until no further precipitation was observed. The solid was purified by silica gel column chromatography with acetone/ NH_4PF_6 (aq, 0.25 M). The counterions were exchanged to Br^- using tetrabutylammonium bromide to yield **An-bOMV** as a yellow solid (220 mg, 17%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.22 (d, $J = 6.4$ Hz, 4H), 8.64 (d, $J = 6.0$ Hz, 4H), 8.52 (d, $J = 6.8$ Hz, 4H), 8.19 (dd, $J = 6.8$, 3.2 Hz, 4H), 7.75 (d, $J = 5.6$ Hz, 4H), 7.45 (dd, $J = 6.8$, 3.2 Hz, 4H), 5.08–4.80 (m, 4H), 4.14–4.07 (m, 8H), 3.92–3.62 (m, 12H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 152.50, 150.66, 146.42, 145.67,

140.44, 125.56, 124.85, 124.43, 122.30, 121.54, 74.80, 69.71, 68.65, 59.80. HR-ESI-MS: m/z 376.1781 ($[M-2Br]^{2+}/2$, calcd for $C_{46}H_{48}N_4O_6^{2+}/2$, 376.1784).

3. Characterization of supramolecular assembly

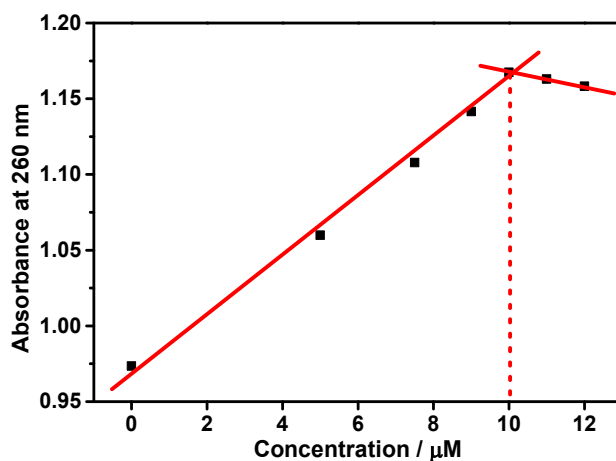


Figure S1. Dependence of the absorbance of **An-bOMV** on the increase of **CB[8]** in water. [**An-bOMV**] = 10.0 μM .

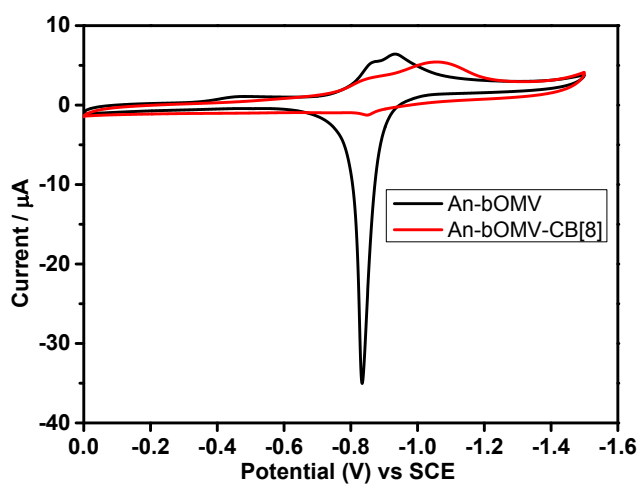


Figure S2. Cyclic voltammograms of **An-bOMV** with and without **CB[8]** in phosphate buffer solution (pH 7.0). Scan rate = 100 mVs^{-1} . [**An-bOMV**] = [**CB[8]**] = 0.1 mM.

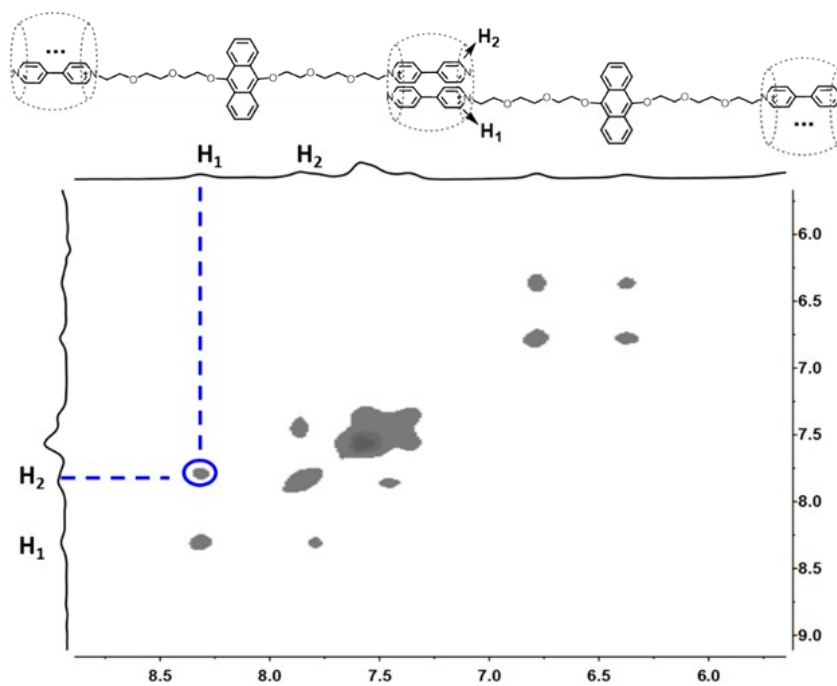


Figure S3. Partial ^1H - ^1H NOESY NMR spectrum of the An-bOMV-CB[8] complex in D_2O .

$[\text{An-bOMV}] = [\text{CB}[8]] = 1.0 \text{ mM}$.

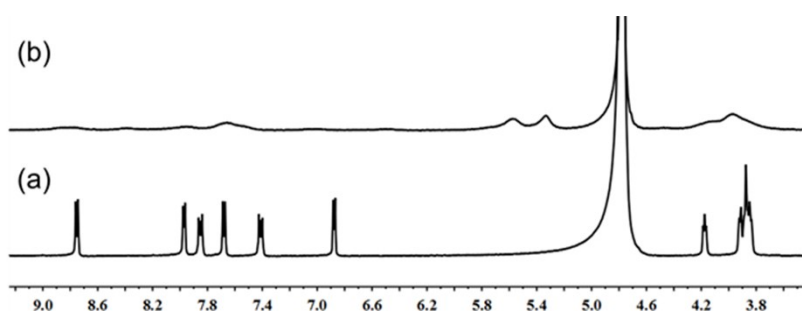


Figure S4. ^1H NMR spectra of (a) An-bOMV and (b) An-bOMV + CB[8] in D_2O . $[\text{An-bOMV}]$

$= [\text{CB}[8]] = 1.0 \text{ mM}$.

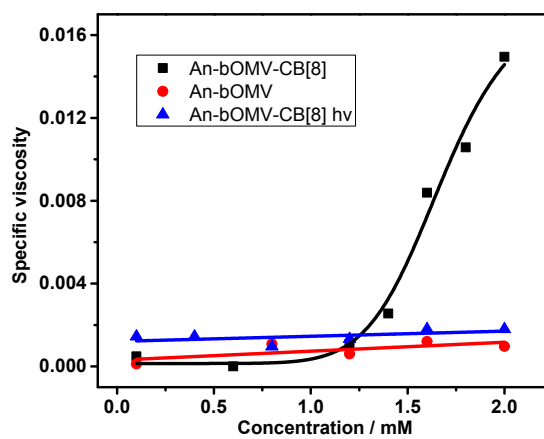


Figure S5. Specific viscosity of aqueous solutions of **An-bOMV**, the **An-bOMV-CB[8]** complex, and the **An-bOMV-CB[8]** complex after light irradiation for 2 h.

4. Characterization of D-A interaction

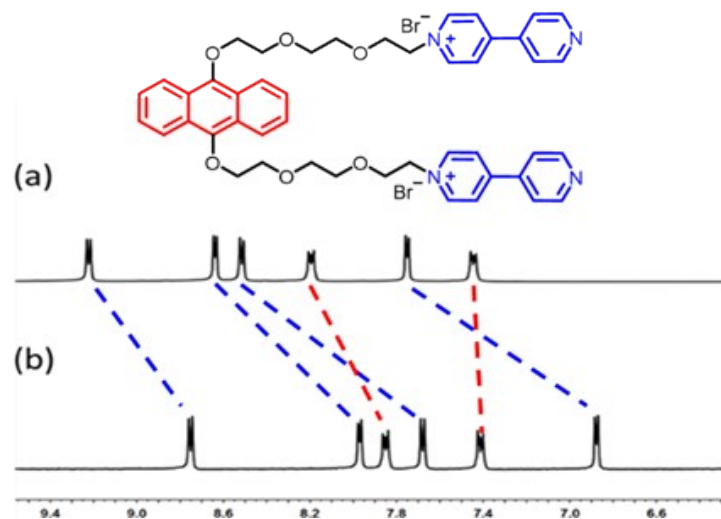


Figure S6. ^1H NMR spectra of (a) **An-bOMV** in $\text{DMSO-}d_6$ and (b) **An-bOMV** in D_2O .

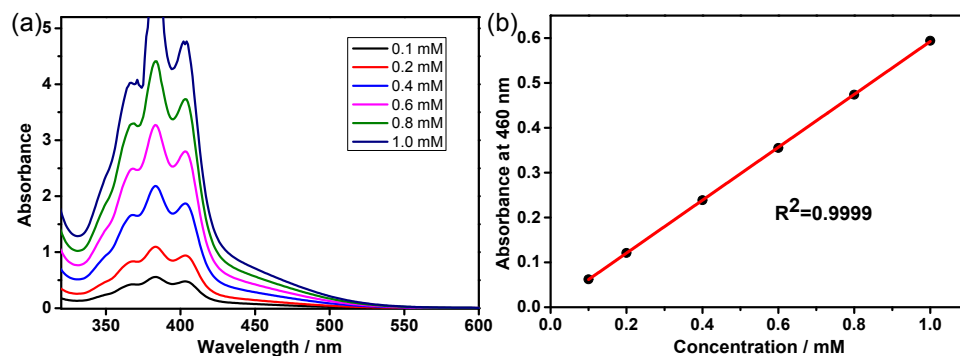


Figure S7. (a) UV-vis absorption spectra of **An-bOMV** in water. (b) The linear fitting of absorbance at 460 nm versus concentration.

5. Light-induced dissipation

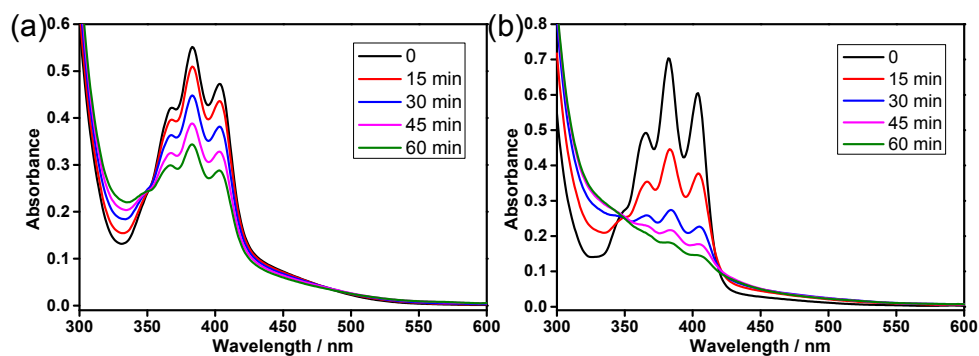


Figure S8. UV-vis absorption spectra of (a) **An-bOMV** and (b) **An-bOMV-CB[8]** assembly under irradiation at pH 7. $[\text{An-bOMV}] = [\text{CB[8]}] = 0.1 \text{ mM}$.

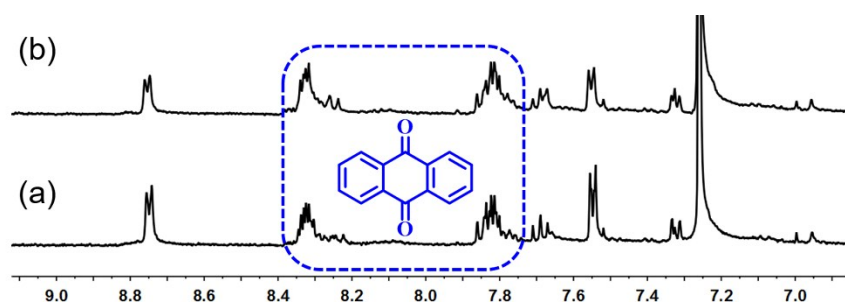


Figure S9. ^1H NMR spectra of the products of (a) **An-bOMV** and (b) **An-bOMV-CB[8]** assembly, in the organic extract phase after irradiation for 2 h in CDCl_3 .

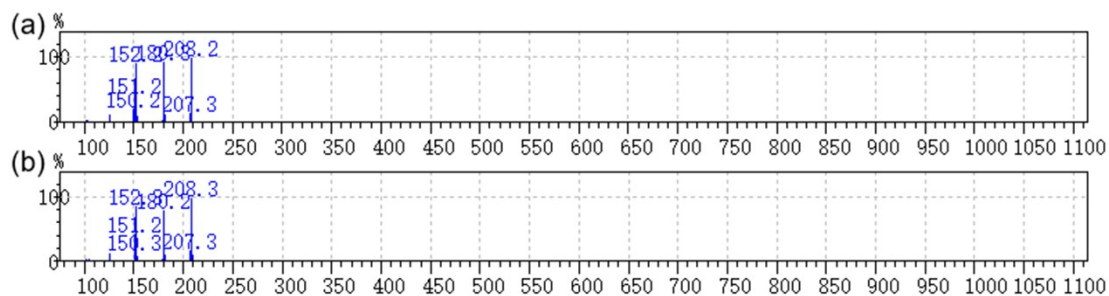


Figure S10. EI-MS spectra of the products of (a) **An-bOMV** and (b) **An-bOMV-CB[8]** assembly in the organic extract phase after irradiation for 2 h.

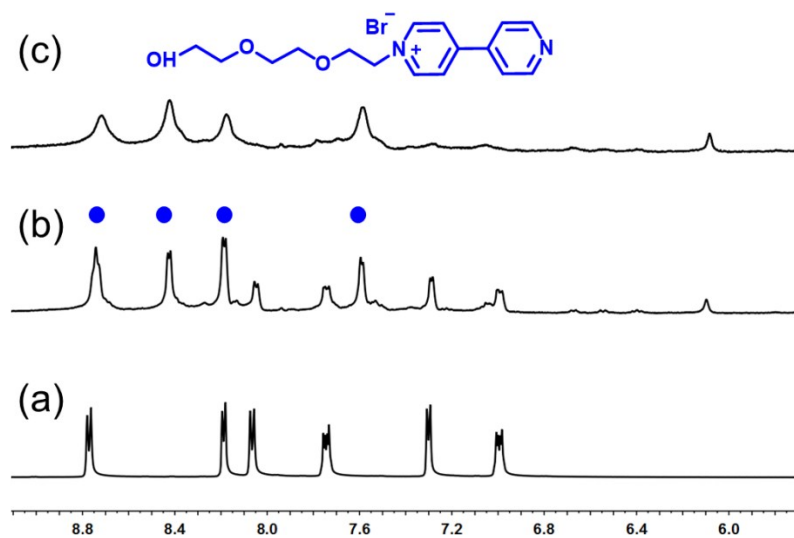


Figure S11. ^1H NMR spectra of (a) **An-bOMV**, and the photolytic products of (b) **An-bOMV** and (c) **An-bOMV-CB[8]** assembly in the water phase after extraction measured in $\text{DMSO-}d_6$. The MV^+ moiety of the resulting alkanol is denoted as symbol ●.

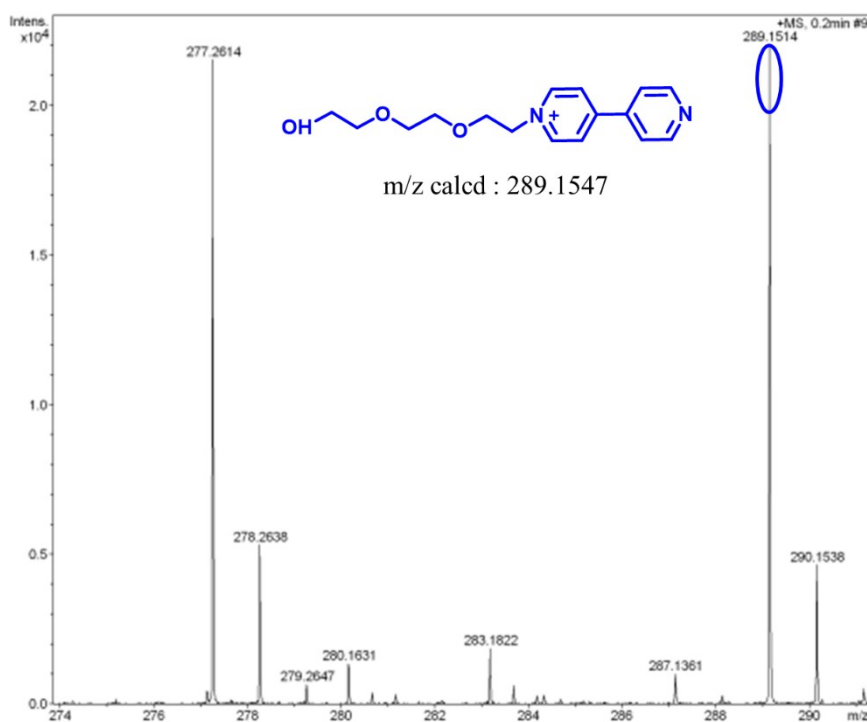


Figure S12. HR-ESI-MS spectrum of the photolytic product of **An-bOMV-CB[8]** assembly in the water phase after extraction.

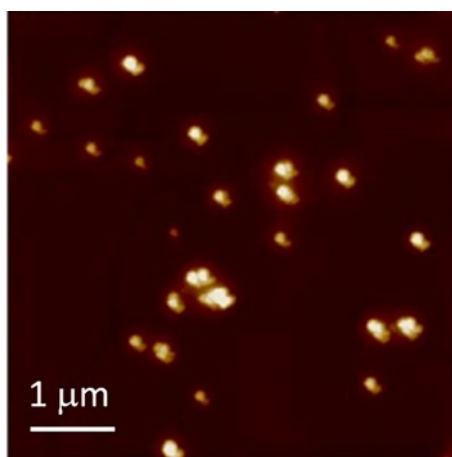


Figure S13. AFM image of An-bOMV-CB[8] assembly after irradiation for 2 h.

6. NMR and Mass spectra of guest molecule

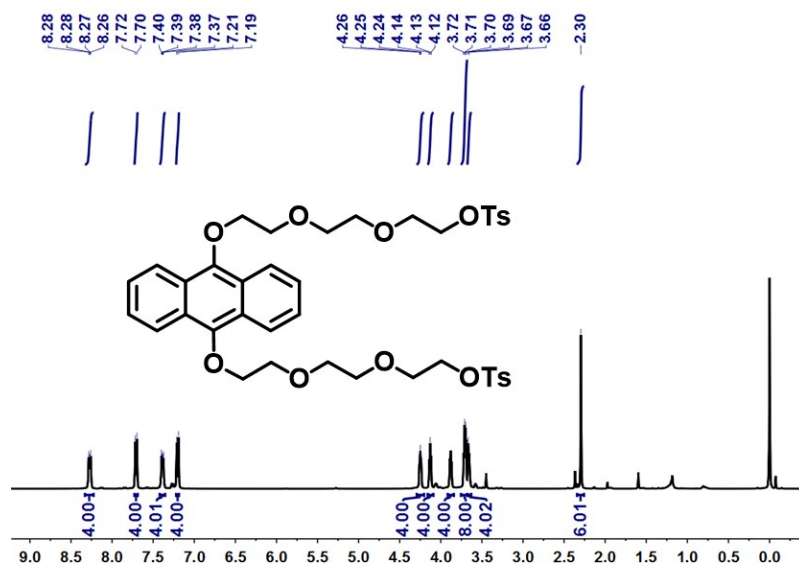


Figure S14. ¹H NMR spectrum of compound **2** in CDCl₃.

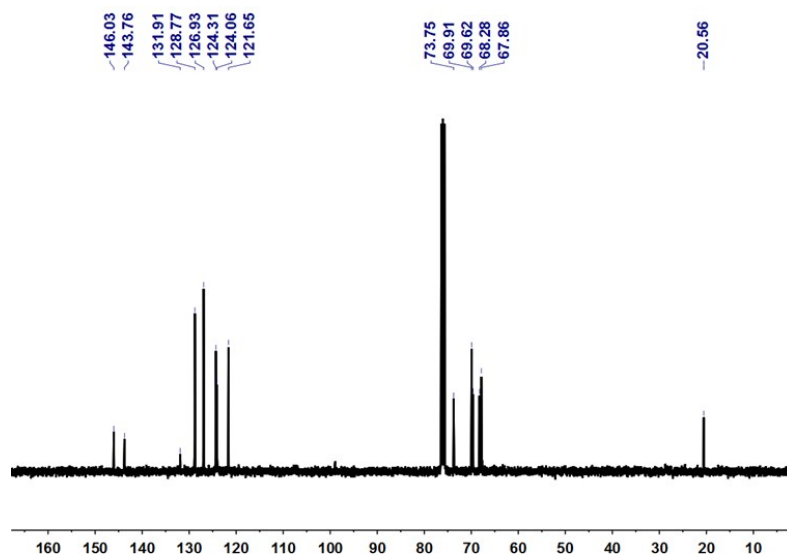


Figure S15. ^{13}C NMR spectrum of compound **2** in CDCl_3 .

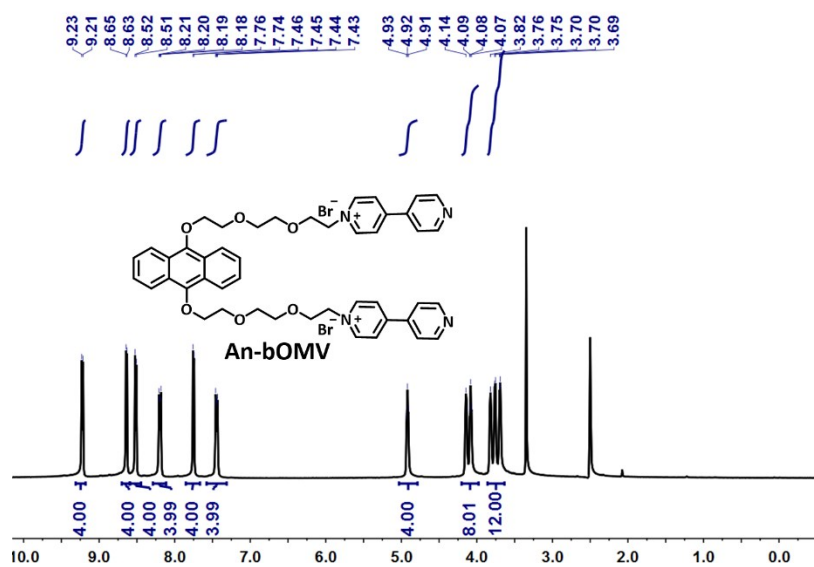


Figure S16. ^1H NMR spectrum of compound **An-bOMV** in $\text{DMSO}-d_6$.

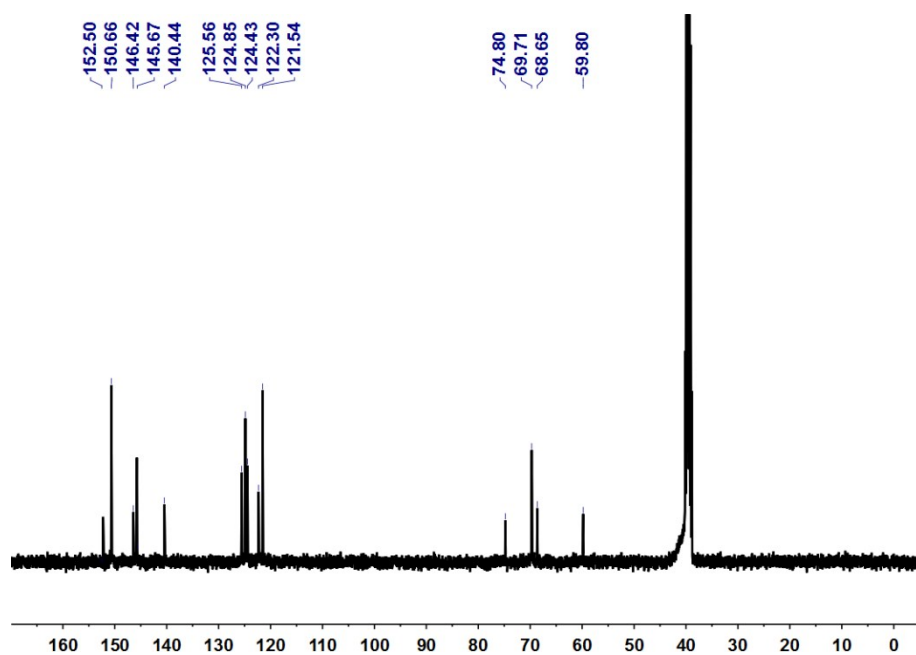


Figure S17. ^{13}C NMR spectrum of compound An-bOMV in $\text{DMSO-}d_6$.

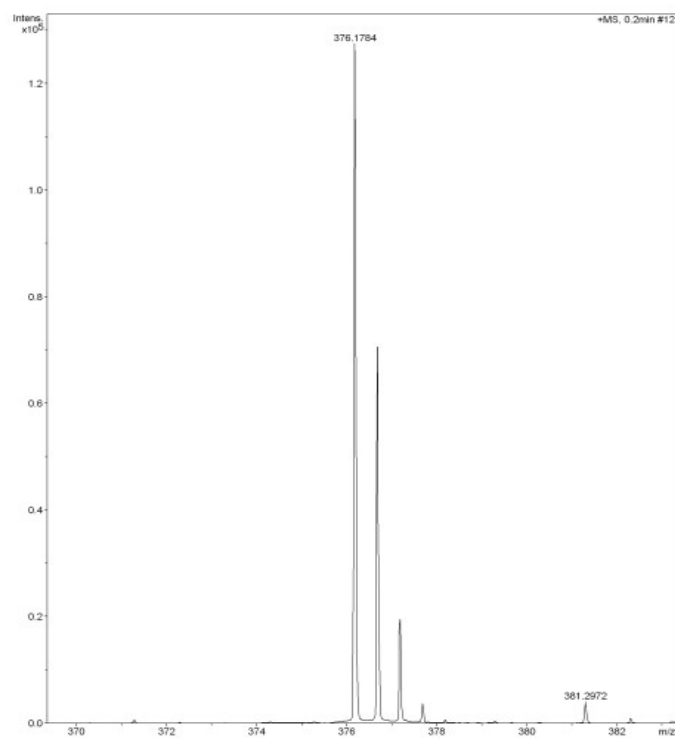


Figure S18. HR-ESI-MS spectrum of compound An-bOMV.

7. Supporting References

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- 2 D. Arian, L. Kovbasyuk and A. Mokhir, *J. Am. Chem. Soc.*, 2011, **133**, 3972–3980.
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