Electronic Supplementary Information

Photolysis of a bola-type supra-amphiphile promoted by water-soluble pillar[5]arene-induced assembly

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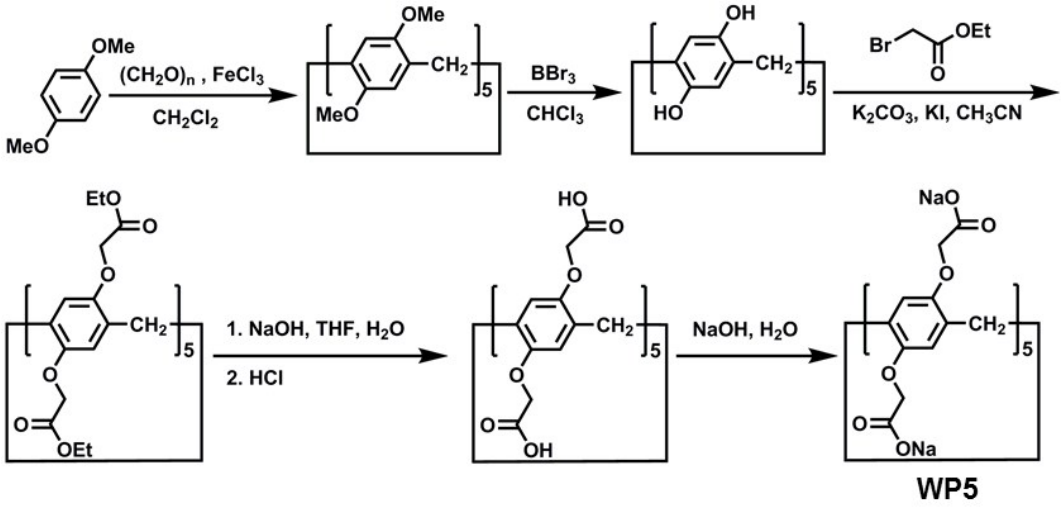
1. *General information*

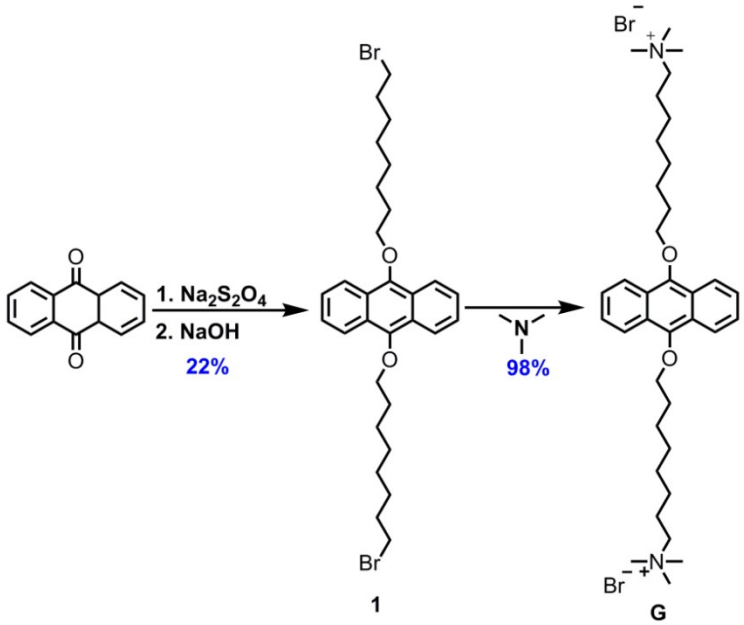
All reactions were performed in air atmosphere unless otherwise stated. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Column chromatography was performed with silica gel (200-300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Transmission electron microscope (TEM) investigations were carried out on a JEM-2100 instrument. Dynamic light scattering (DLS) measurements were carried out on a Brookhaven BI-9000AT system (Brookhaven Instruments Corporation, USA) equipped with a 200 mW laser light and operating at λ = 514 nm. ζ-potential measurement was performed at 25 °C on a Zeta sizer-Nano Z (Malvern Instruments Ltd., Worcestershire, UK) using the Smoluchowski model for the calculation of the ζ-potential from the measured electrophoretic mobility. The UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV-Vis Spectrometer. The excitation and emission spectra were recorded on a Hitachi F-7000 Fluorescence Spectrometer. Melting points (M.p.) were determined using a Focus X-4 apparatus (made in China) and were not corrected.

2. *The syntheses of WP5* and *G*

WP5 was synthesized and purified according to previously reported procedures (Scheme S1).[S1]



Scheme S1. The synthesis route of **WP5**.



Scheme S2. The synthesis route of **G**.

1: Under Ar protection, 9,10-anthraquinone (0.416 g, 2 mmol), $Na_2S_2O_4$ (2.08 g , 12 mmol), and cetyl trimethyl ammonium bromide (0.032 mL, 0.1 mmol) were desolved in a mixture of Ar-saturated DI water (6 mL) and THF (10 mL). After stirred for 15

min at 25 °C, a solution of KOH (1.12 g, in 10 mL water) was added. Then, the obtain solution were added dropwisely to 1,8-dibromooctane and heated to 80 °C. The resulting solution was stirred at 80 °C for 8 h. Then the organic phases were separated, dried over $MgSO_4$, and concentrated to get the oily crude product, which was added to *n*-hexane (200 mL) and filtered. The obtained filtrate was concentrated and finally purified by column chromatography with n-hexane/CH_2Cl_2 (from 100/1 to 60/1, *v/v*) as the eluent to give the target Compound **1** as yellow solid (0.26 g, 0.44 mmol, 22%). M.p. 65-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.27 (d, *J* = 8 Hz, 4H, anthracene-*H*), 7.48 (d, *J* = 8 Hz, 4H, anthracene-*H*), 4.16 (t, *J* = 4 Hz, 4H, -C***H***(O)-), 3.44 (t, *J* = 4 Hz, 4H), 2.08-2.02 (m, 4H), 1.92-1.88 (m, 4H), 1.67-1.53 (m, 4H), 1.52-1.45 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) *δ* (ppm) = 147.5, 125.17, 125.15, 122.7, 76.1, 34.0, 32.8, 30.6, 29.4, 28.8, 28.2, 26.2. HR-ESI-MS: m/z Calcd for $C_{30}H_{40}Br_2O_2Na$ $[M+Na]^+$ 615.2167, found 615.2170.

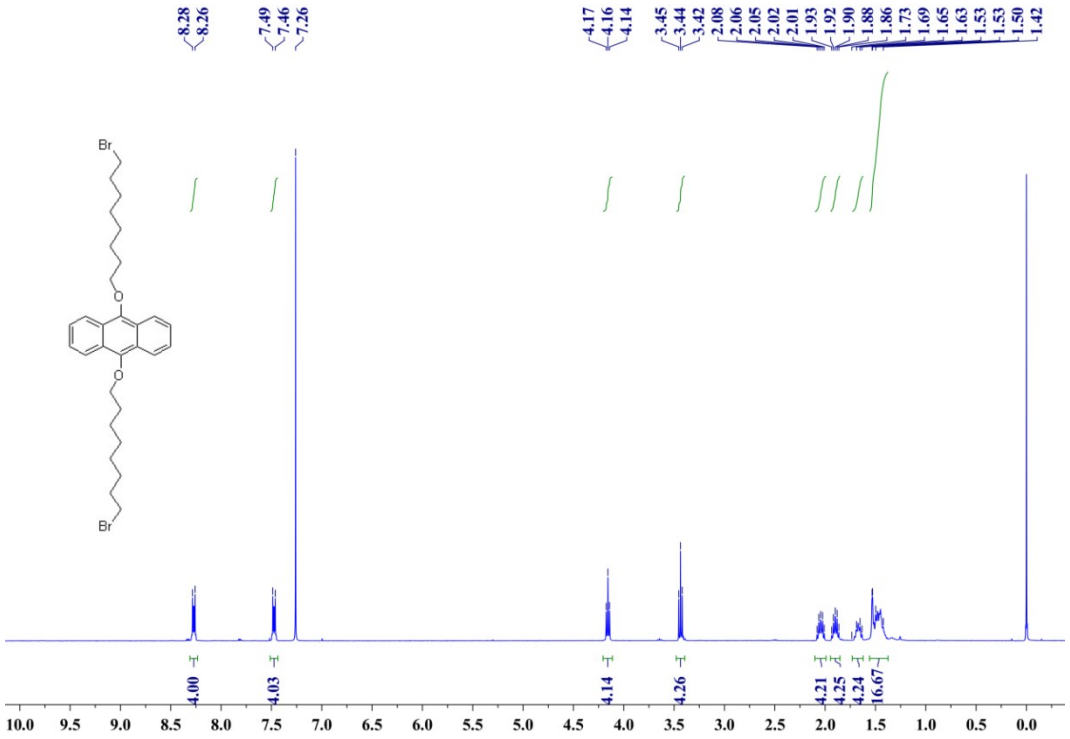


Fig. S1 ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$, 298 K).

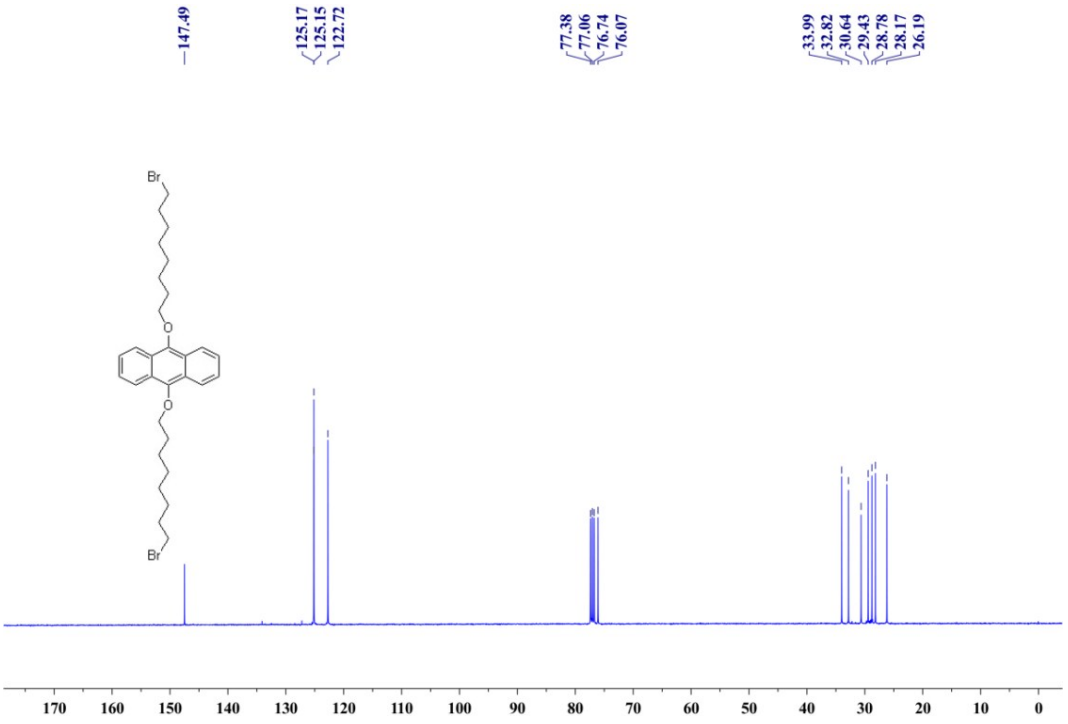


Fig. S2 ^{13}C NMR spectrum of **1** (100 MHz, $CDCl_3$, 298 K).

G: Compound **1** (0.07 g, 0.12 mmol) was dissolved in a $CHCl_3$ (2 mL) in a schlenk flask, and trimethylamine (33% in ethanol, 1 mL) was added. The resulting solution was refluxed for 24 h. Then, the mixture was concentrated under reduced pressure and the obtained residue was dissolved in a small amount of anhydrous MeOH (1 mL), which was then added dropwise to plenty of diethyl ether (150 mL), the precipitates was collected by filtration, washed by diethyl ether and dried in vacuum, and the target guest compound **G** was obtained as a yellow solid (0.08 g, 0.118 mol, 98%). M. p. 164-166 °C. ^{1}H NMR (400 MHz, CD_3OD, 298 K) δ (ppm) = 8.26 (d, *J* = 8 Hz, 4H, anthracene-*H*), 7.50 (d, *J* = 8 Hz, 4H, anthracene-*H*), 4.16 (t, *J* = 8 Hz, 4H, -C***H***(O)-), 3.38-3.33 (m, 4H), 3.30 (s, 18H), 2.09-2.04 (m, 4H), 1.84-1.82 (m, 4H), 1.82-1.75 (m, 4H), 1.56-1.53 (m, 8H), 1.48-1.46 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD, 298 K) δ (ppm) = 147.2, 125.1, 125.0, 122.3, 75.8, 66.5, 52.2, 30.2, 29.1, 28.8, 25.9, 22.6. HR-ESI-MS: m/z Calcd for $C_{36}H_{58}N_2O_2$ $[M-2Br]^{2+}$ 275.2244, found 275.2239.

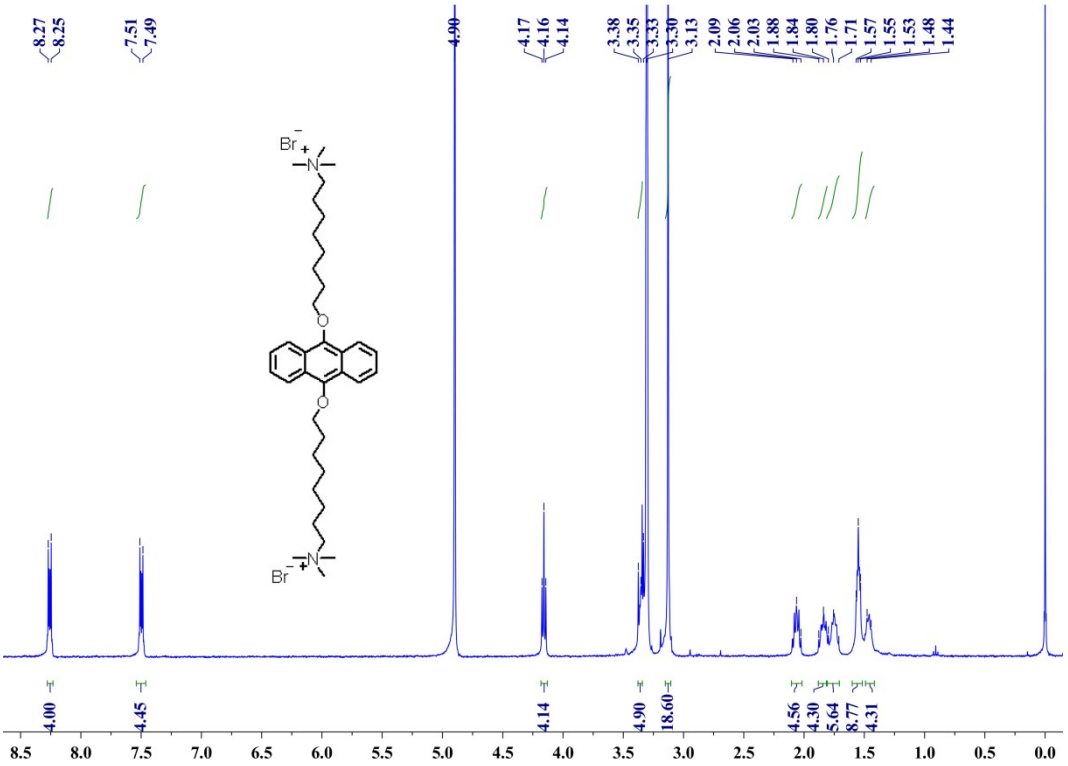


Fig. S3 ^{1}H NMR spectrum of **G** (400 MHz, CD_3OD, 298 K).

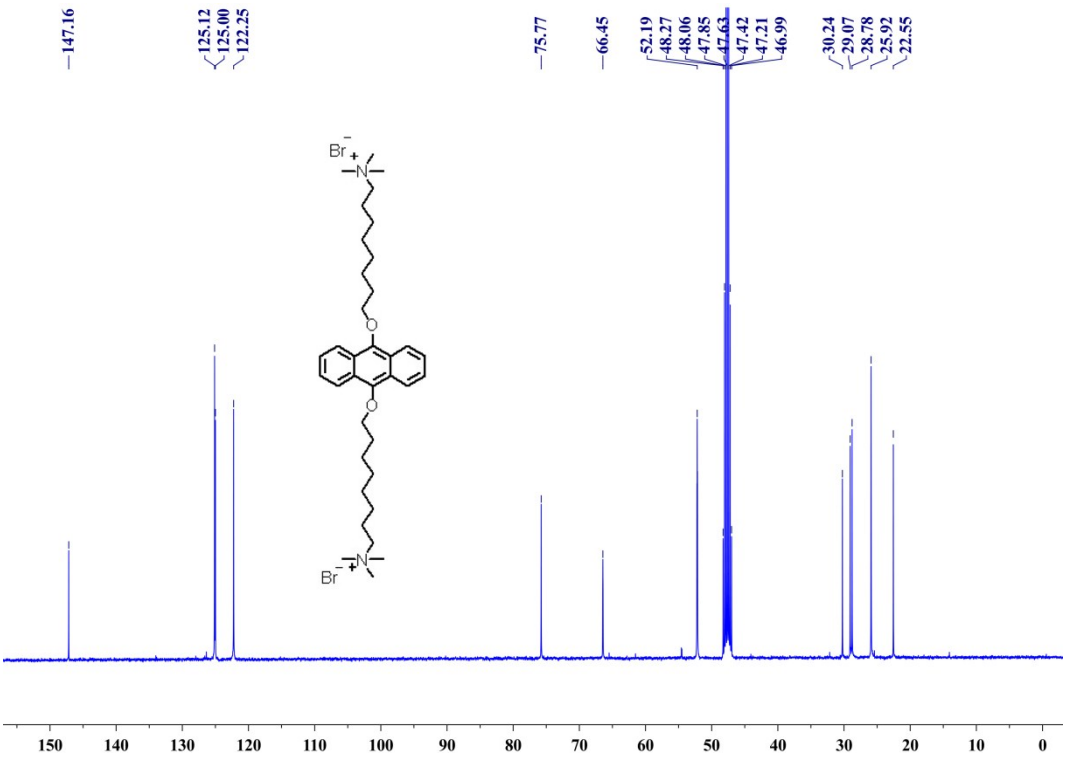


Fig. S4 ^{13}C NMR spectrum of **G** (100 MHz, CD_3OD, 298 K).

3. *Self-assembly of WP5 and G in water*

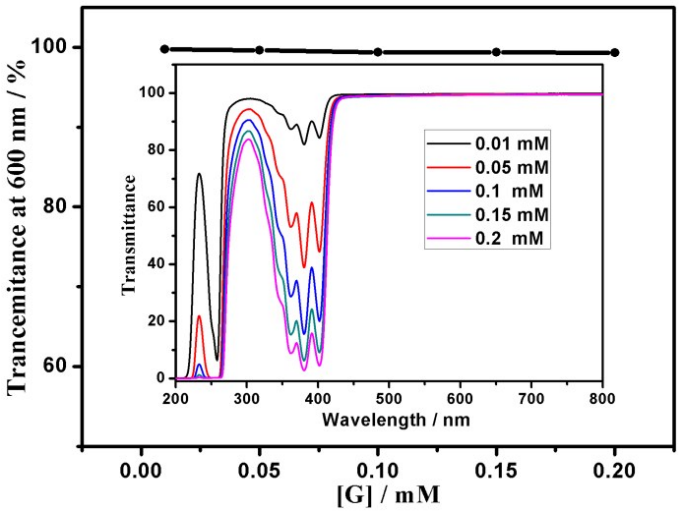


Fig. S5 Dependence of the optical transmittance at 600 nm on the concentration of **G**. Inset: optical transmittance of the aqueous solutions of **G** at different concentrations at 25 °C.

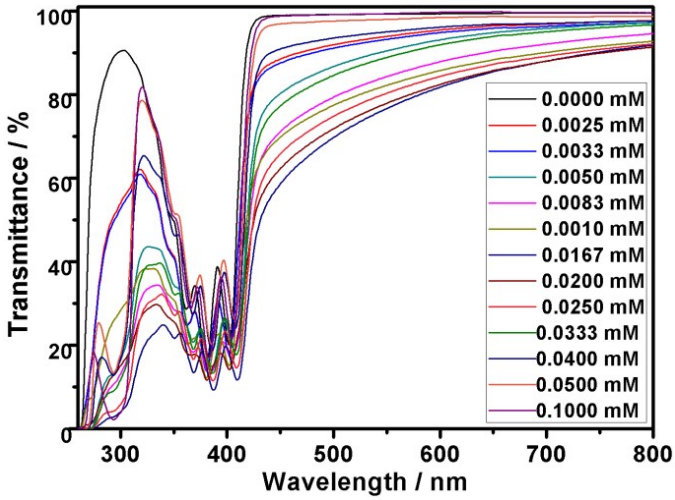


Fig. S6 Optical transmittance of **G** (0.10 mM) upon increasing the concentration of **WP5** (0 − 0.10 mM) at 25 °C in water.

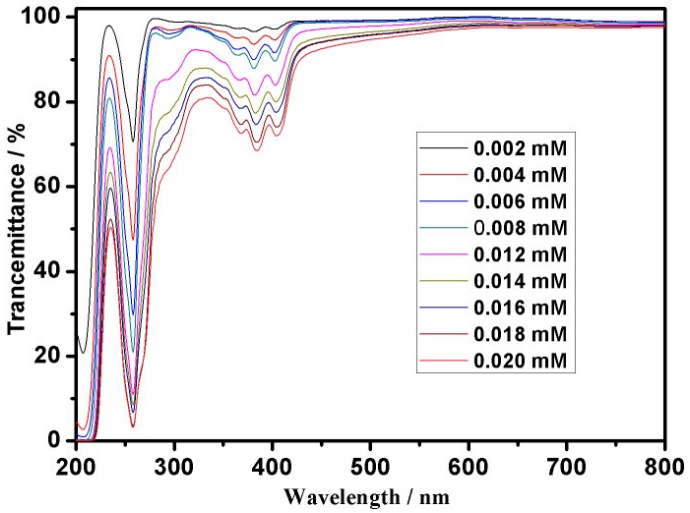


Fig. S7 Optical transmittance of the **WP5-G** assembly at a fixed molar ratio of [**G**]/[**WP5**] = 6/1 at different concentrations from 0.002 mM to 0.02 mM.

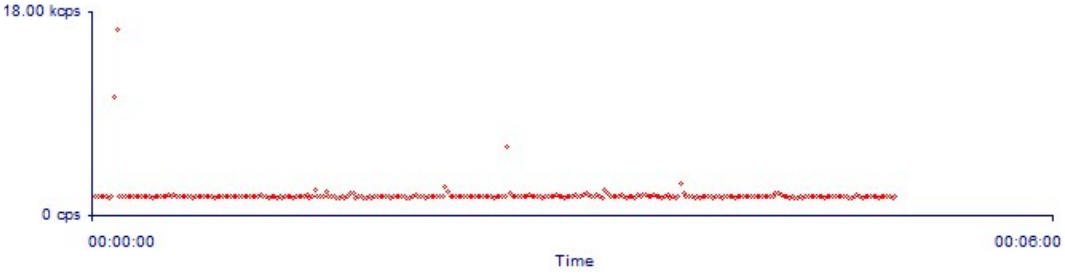


Fig. S8 DLS data of **G** (0.1 mM) at 25 °C in water.

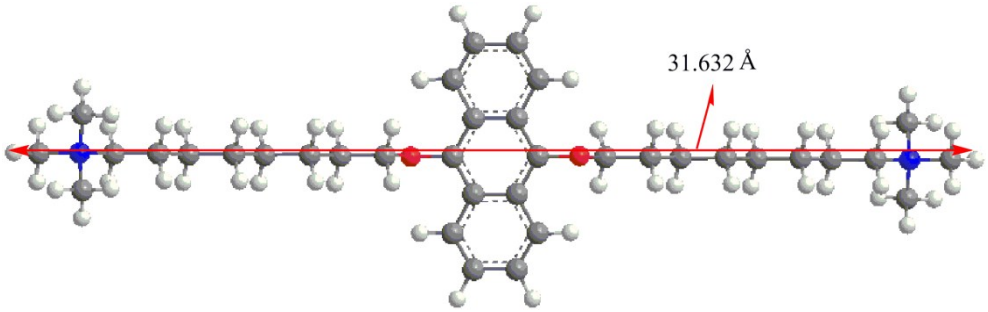


Fig. S9 The geometries and frequencies of the **G** is calculated using M062X method with 6-311 + **G** (2d, p) basis.[S2] (Compound **G** is identified for minima, number of imaginary frequencies is zero). All calculations are performed by using the Gaussian 09 program.[S3]

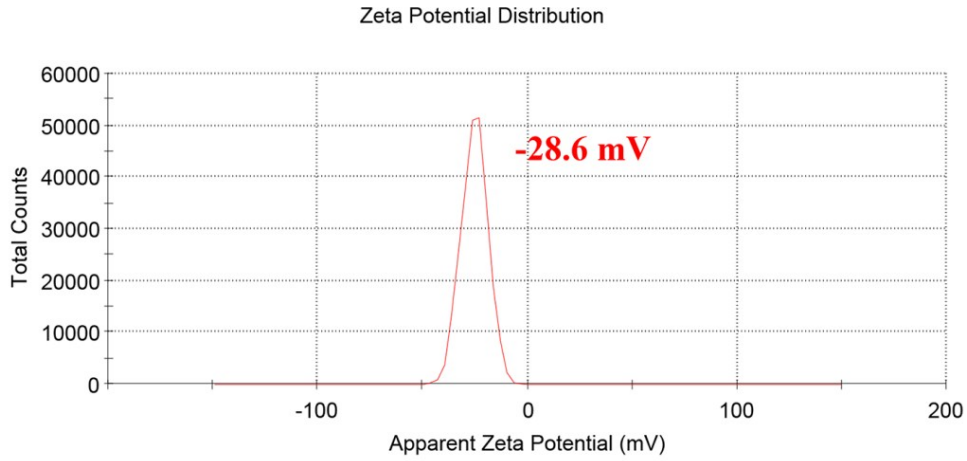


Fig. S10 The zeta potential of the **WP5**-**G** assembly. [**WP5**] = 0.0167 mM, and [**G**] = 0.10 mM.

4. Host-guest complexation of WP5 and G

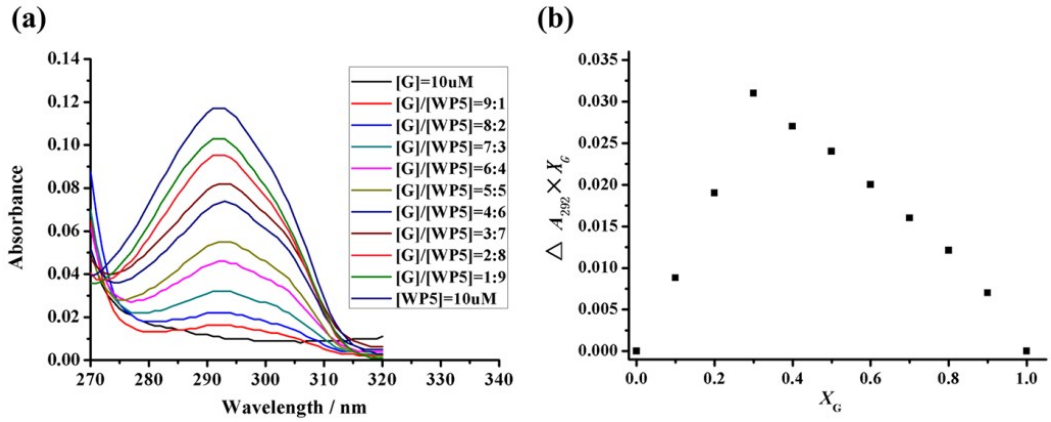


Fig. S11 (a) UV-Vis absorption spectra of complex (**WP5**)$_2$⊃**G** with different molar ratios in water while [**WP5**] + [**G**] = 10 μM. (b) Job plots of the complex (**WP5**)$_2$⊃**G** showing a 2:1 stoichiometry between **WP5** and **G** by plotting the absorbance differences at 292 nm (a characteristic absorption peak of **WP5**) against the mole fraction of **G**.

5. *UV-Vis photolysis of the WP5-G assembly*

The preparation methods for free **G** and the assembled **G** were as follows: firstly, the water solution of free **G** (2×10^{-4} mol/L) was prepared. Then, for investigating the photocleavage rate of free **G**, the mother liquor of free **G** was diluted to different concentrations, and 3 mL of each diluted solution was placed in a centrifugal tube and further irradiated by UV light at 365 nm for 30 min under air at room temperature. For investigating the photocleavage rate of the assembled **G**, the aqueous solution of free **G** (25 mL, 2×10^{-4} mol/L) was added to a volumetric flask (50mL), then **WP5** (2 mL, 4.167×10^{-4} mol/L) was added quickly, and finally some water was added until the volume of the solution reached 50 mL. 3 mL of the assembled **G** solution was placed in a centrifugal tube and further irradiated by UV light at 365nm for 30 min under air at room temperature.

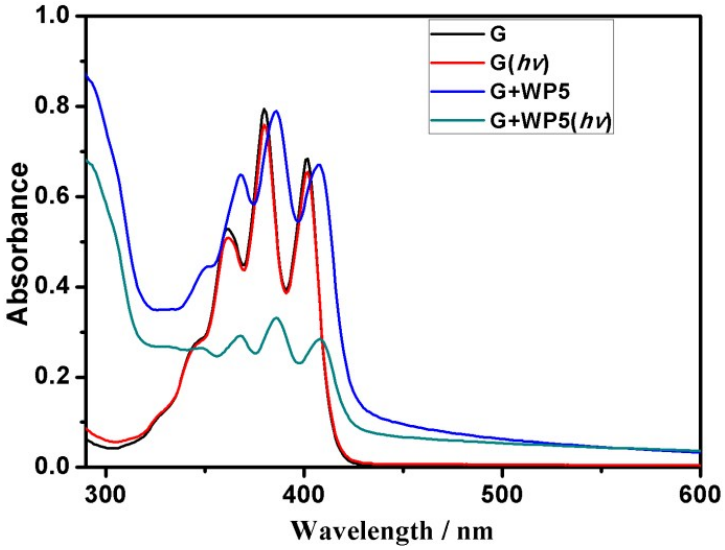


Fig. S12 UV-Vis absorption spectra of **G** (0.10 mM), **WP5-G** assembly, **G** after UV irradiation at 365 nm for 30 min, and the **WP5-G** assembly after UV irradiation at 365 nm for 30 min.

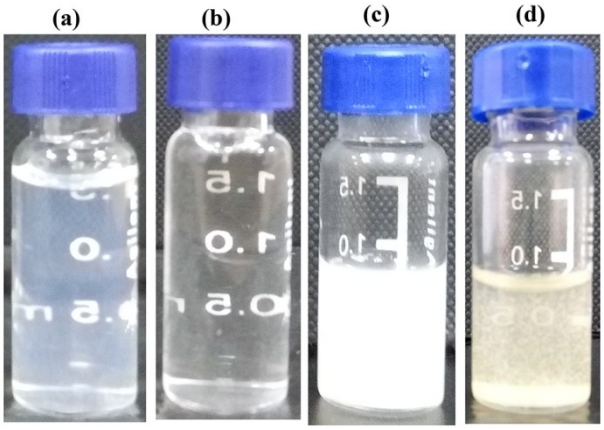


Fig. S13 Photograph of the solution of **WP5-G** assembly ([**G**] = 0.10 mM, [**G**]/[**WP5**] = 6/1) before (a) and after (b) UV irradiation for 30 min; and the solution of **WP5-G** assembly ([**G**] = 2 mM, [**G**]/[**WP5**] = 2/1) before (c) and after (b) UV irradiation for 30 min.

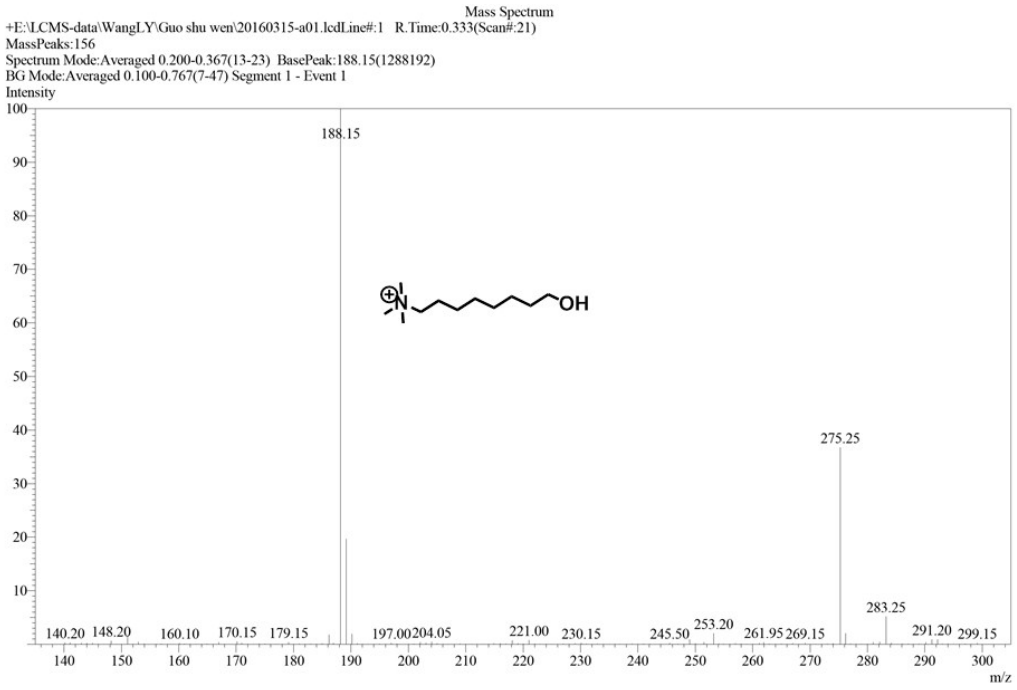


Fig. S14 ESI-MS spectrum of the **WP5-G** assembly upon UV irradiation at 365 nm for 30 min.

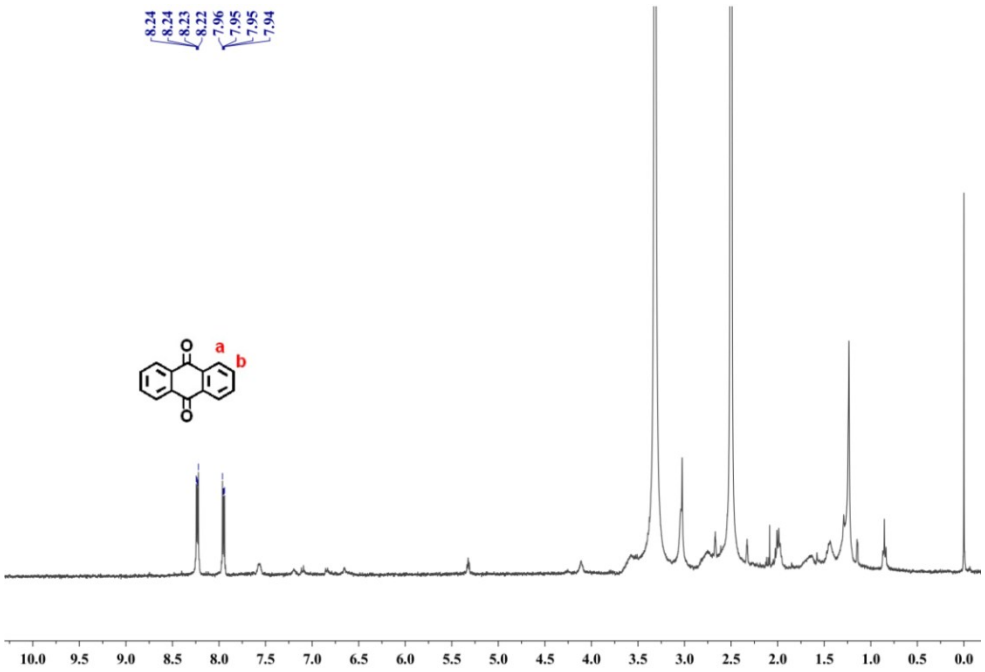
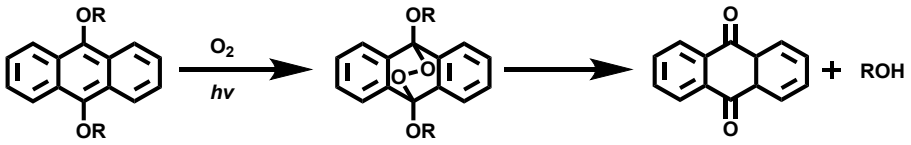


Fig. S15 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of the precipitate generated in the solution of **WP5-G** assembly upon UV irradiation at 365 nm for 30 min.



Scheme S3. Proposed mechanism for the photooxidation and further decomposition of 9,10-dialkoxyanthracene.

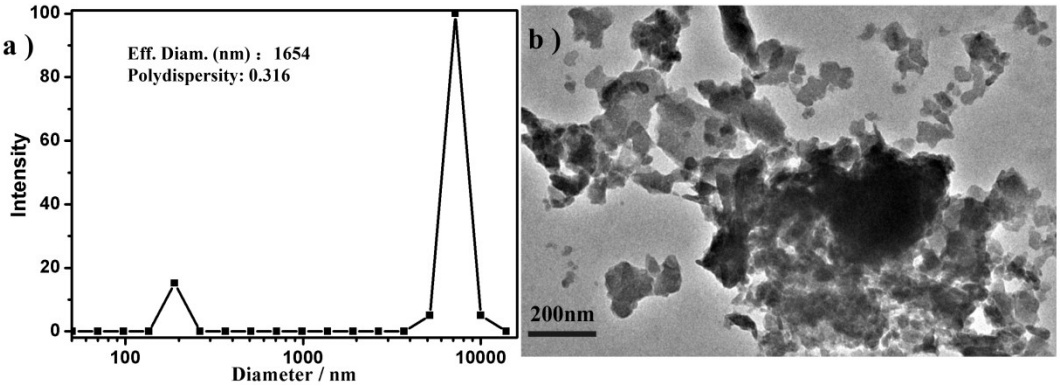


Fig. S16 (a) DLS data and (b) TEM image of the **WP5-G** assembly upon UV irradiation at 365 nm for 30 min.

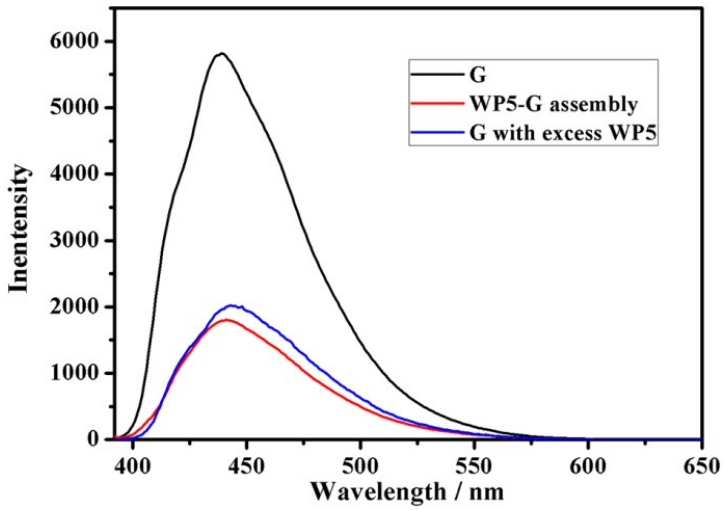


Fig. S17 Fluorescence spectra of **G** (0.1 mM), **WP5-G** assembly, and the mixture of **G** (0.10 mM) with excess amount of **WP5** (0.40 mM) at 25 °C (λ_{ex} = 365 nm).

6. Visible light-responsiveness of the WP5-G assembly

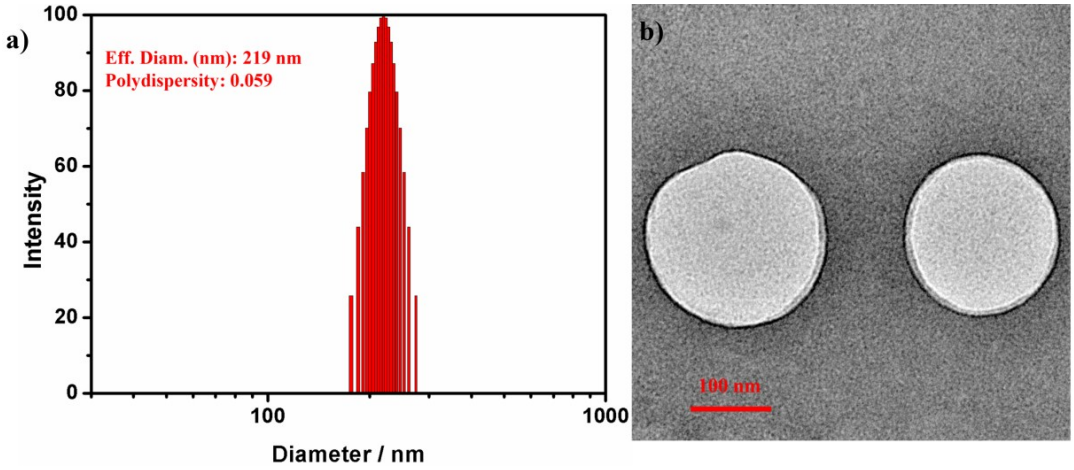


Fig. S18 (a) DLS data of the **WP5-G** assembly with ESY (0.003 mM) coassembling at 25 °C. (b) TEM image of the **WP5-G** assembly with ESY (0.003 mM) coassembling.

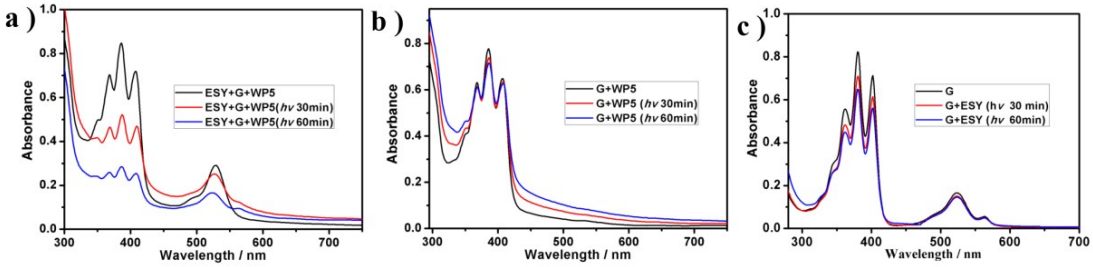


Fig. S19 UV-Vis absorption spectra of the **WP5-G** assembly in the presence (a) and absence (b) of ESY (0.003 mM), and (c) the UV-Vis absorption spectra of **G** in the presence of ESY (0.003 mM) upon irradiation with visible light at 525 nm for different time.

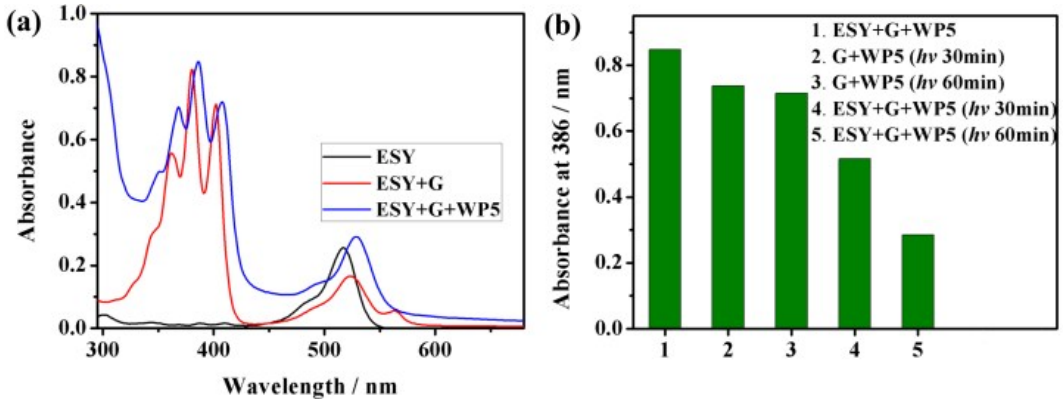


Fig. S20 (a) UV-Vis absorption spectra of ESY (0.003 mM), **G** (0.1 mM) with eosin (0.003 mM), **WP5-G** aggregates with ESY (0.003 mM) (containing 0.5% DMSO). (b) Absorbance at 386 nm of the **WP5-G** aggregate and the **WP5-G** aggregates with ESY (0.003 mM) upon irradiation at 525 nm for different times.

7. ^{1}H NMR studies on the detailed complex structure of the formed supra-amphiphile

A mixture of **[WP5]**/**[G]** = 2:1 was studied for comparison with the **WP5-G** aggregates formed at a molar ratio of **[WP5]**/**[G]**= 1:2, since the signals of the aggregates formed at the best molar ratio broadened severely and was unidentifiable and/or undetectable. Upon adding 2 equiv. of **WP5** into the **G** solution, the signals of

$H_{b\text{-}e}$ on **G** shifted upfield remarkably due to the shielding effect of the electron-rich cavity of **WP5** (Fig. S21b), reflecting the inclusion of the alkyl chain of **G** into the hydrophobic **WP5** cavity.[S4] Meanwhile, the signals of anthracene group shifted downfield, which might be due to the deshielding effect of the aromatic ring of **WP5** after inclusion with **G**. However, when only 0.5 equiv. of **WP5** was added into **G** solution, the threaded signals of $H_{b\text{-}e}$ on **G** could also be detected, and the signals of anthracene group became more broad and complicated due to the π-π stacking effect (Fig. S21c), indicating the occurrence of **WP5**-induced aggregation process.

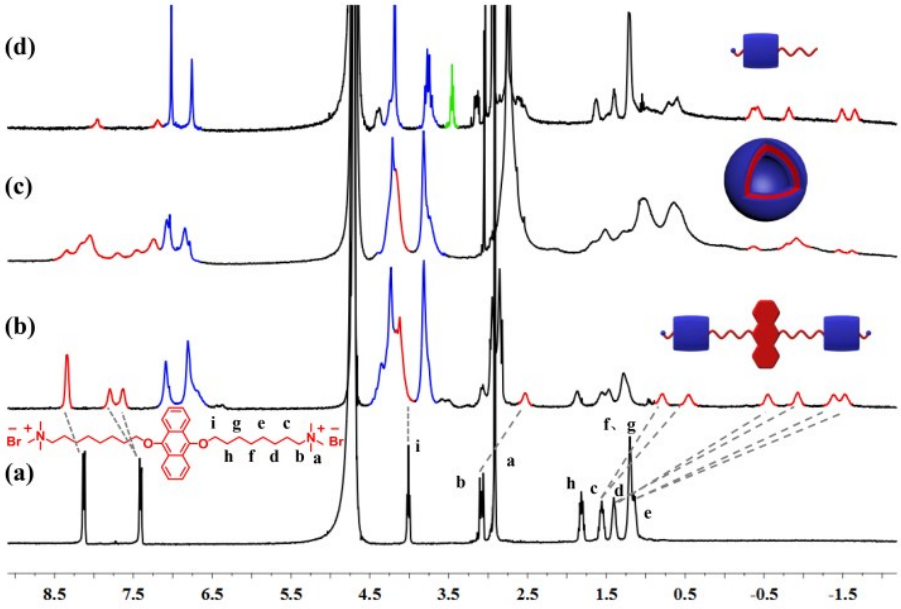


Fig. S21 ^{1}H NMR spectra of (a) **G**, (b) **WP5** + **G** ([**WP5**]/[**G**] = 2/1), (c) the assembly formed by **WP5** and **G** ([**WP5**]/[**G**] = 1/2), and (d) the **WP5-G** aggregates after UV irradiation (365 nm) for 20 min in D_2O ([**G**] = 2.0 mM).

8. References

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S2. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215-241.

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