Supporting Information

Expected and unexpected photoreactions of 9-(10-)substituted anthracene derivatives in cucurbit[*n*]uril hosts

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General Experimental Section.

CB[8], CB[10], guest **G1**, **G2**, **G3** (as chloride salt) were prepared according to literature procedures.[1-5] All ^{1}H and ^{13}C NMR spectra were collected on Agilent 600 MHz DD2. UV/Vis were performed on a SHIMADZU UV-3600 instrument with 1 cm pathlength cells at 298 K. Fluorescence spectra were collected on a PerkinElmer LS-55 machine. ESI-MS were performed on a Solarix 9.4T. EI were detected on a Waters GCT 8000. 9-anthracenemethanol and anthraquinone, used as standard samples, were purchased from Aladdin. The MMFF modeling was performed by Spartan ’14.

References:

1 Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem*., 2001, **66**, 8094-8100.

2 X. Yang, Z. Zhao, X. Zhang and S. Liu, *Sci. China Chem*., 2018, **61**, 787-791.

3 Z.-H. Chen, F.-G. Zhou, Y.-Q. Zhang, Q.-J. Zhu, S.-F. Xue and Z. Tao, *J. Mol. Struct*., 2009, **930**, 140-146.

4 G. Masafumi, M. Takashi, S. Masamitsu and K. Hiromasa, *B. Chem. Soc. Jpn*., 2000, **73**, 97-105.

5 J. Zhang, Y. Liu, B. Yuan, Z. Wang, M. Schönhoff and X. Zhang, *Chem. Eur. J*., 2012, **18**, 14968-14973.

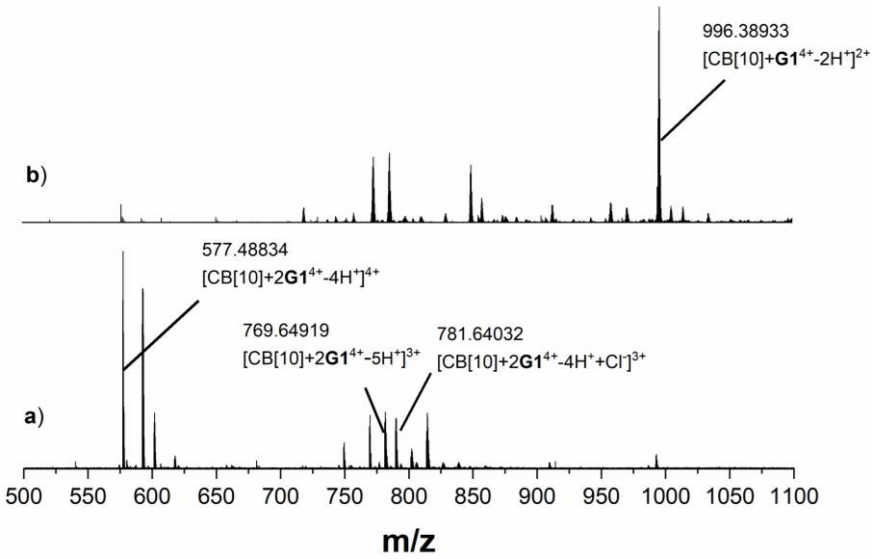


Fig. S1 ESI-MS spectra of: a) 2:1 mixture of **G1** and CB[10]; b) **G1** with excess CB[10].

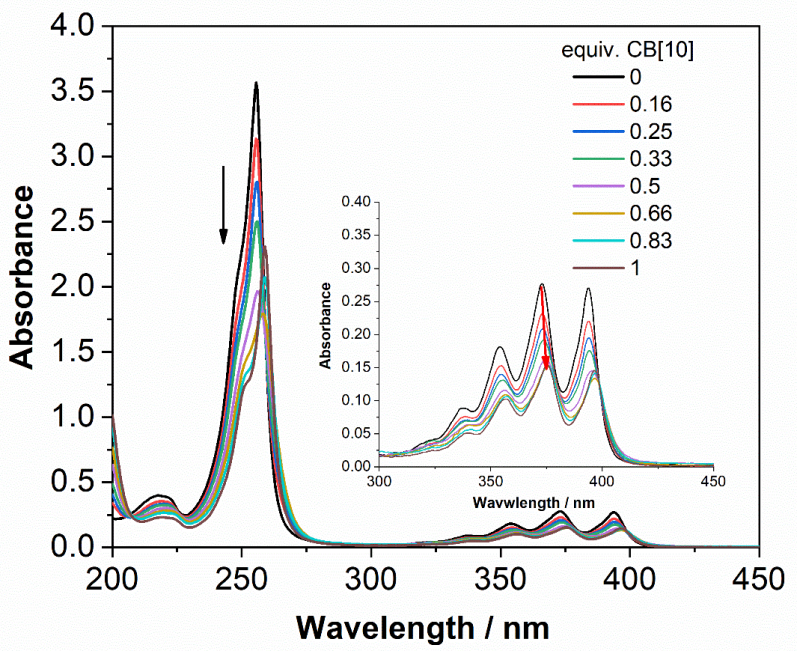


Fig. S2 UV/Vis spectra of **G1** (31.25 µM) with addition of CB[10] (0-1 equiv.).

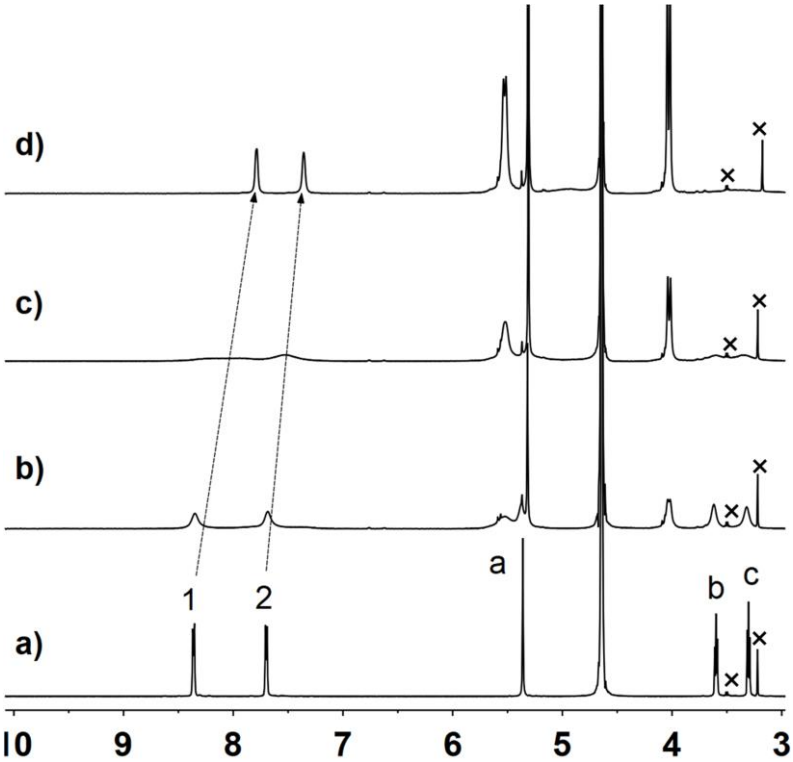


Fig. S3 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) free **G1** (2.5 mM); b) 4:1 mixture of **G1** and CB[8]; c) 2:1 mixture of **G1** and CB[8]; d) 1:1 mixture of **G1** and CB[8] (proton signals of impurities are marked with '×').

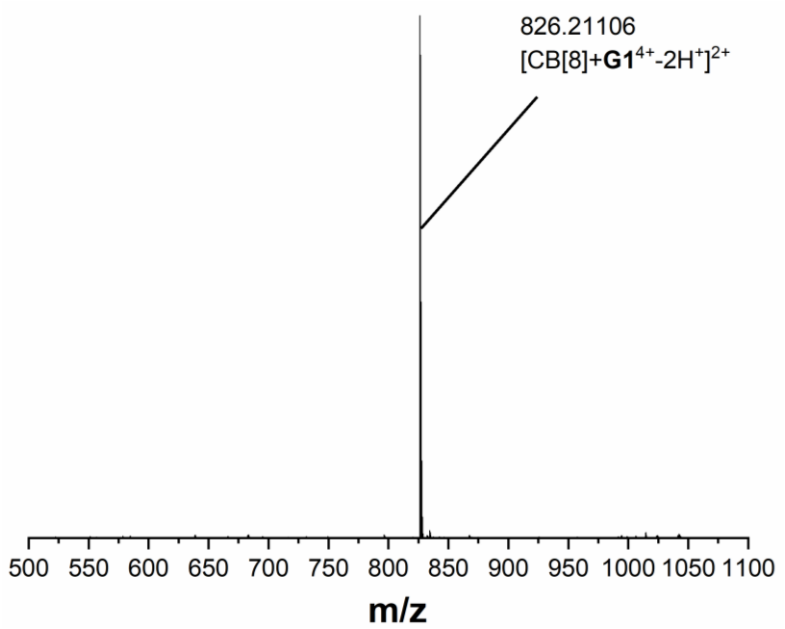


Fig. S4 ESI-MS spectrum of 1:1 mixture of **G1** and CB[8].

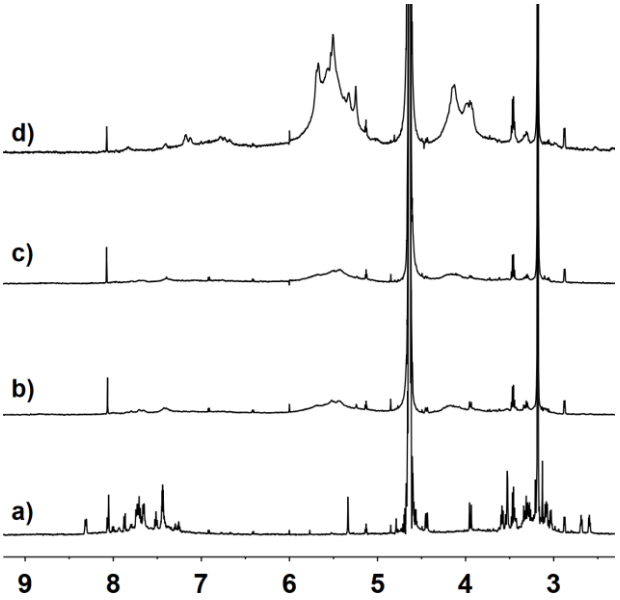


Fig. S5 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of **G1** solution (2.5 mM) after UV irradiation for 12 h with, a) without CB[10]; a) 0.25 equiv. of CB[10]; c) 0.5 equiv. of CB[10]; d) 1.0 equiv. of CB[10].

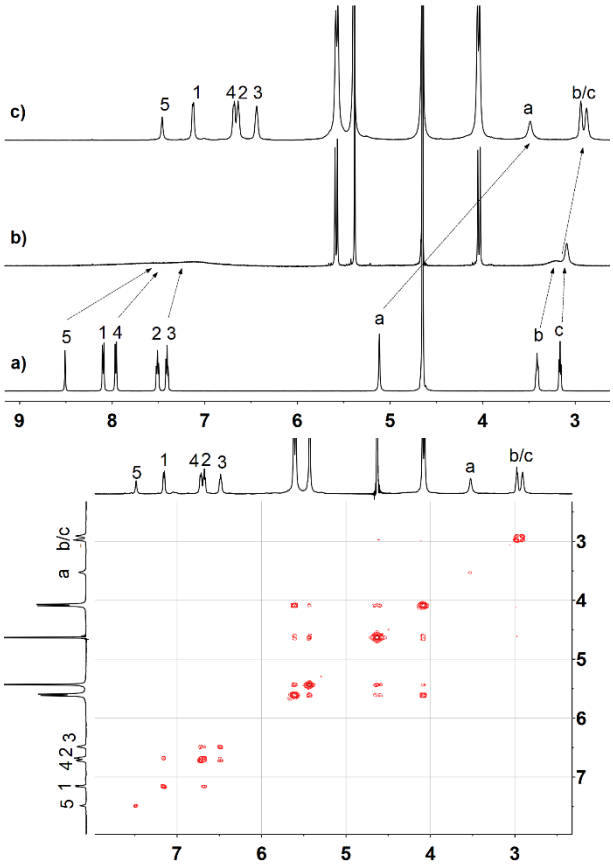


Fig. S6 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of a) free **G2** (2.5 mM), b) 4:1 mixture of **G2** and CB[10], c) **G2** and excess CB[10] (top), and partial COSY NMR spectrum of **G2** and excess CB[10] (bottom).

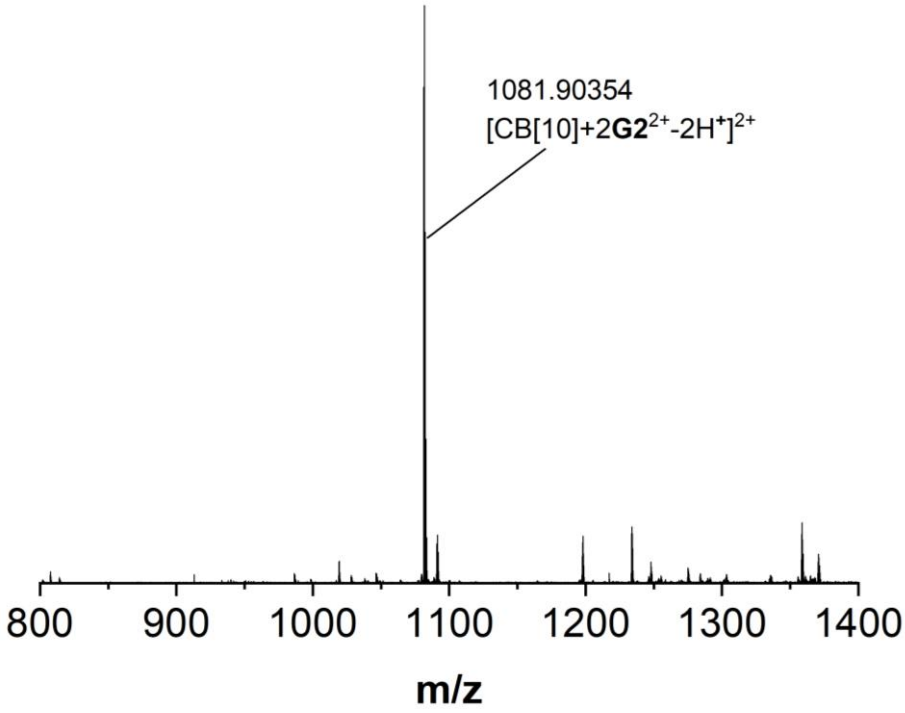


Fig. S7 ESI-MS spectrum of **G2** with excess CB[10].

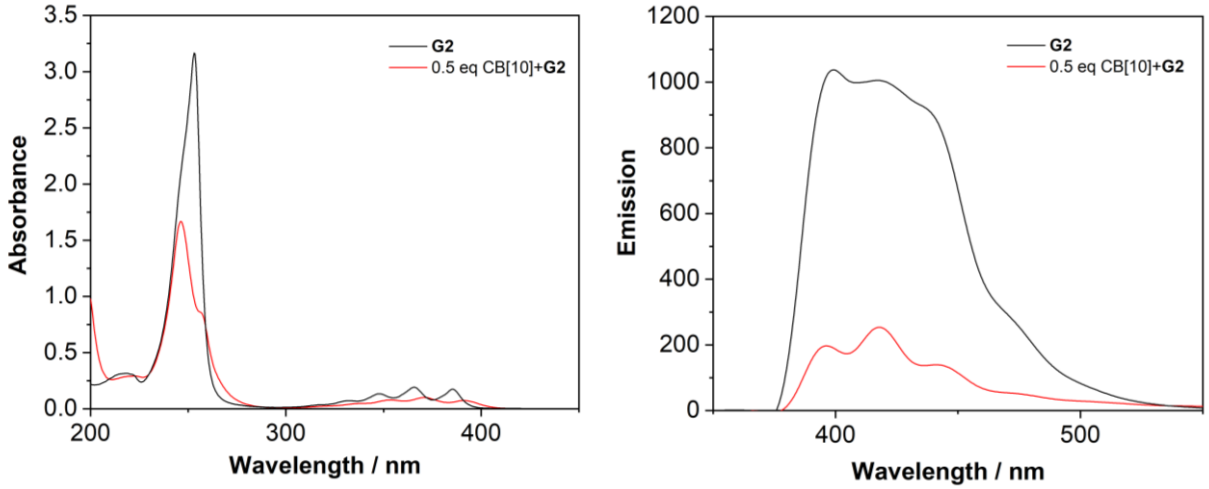


Fig. S8 UV/Vis spectra and fluorescence emission spectra of **G2** (31.25 µM) with addition of CB[10] (0.5 equiv.) (λ_{ex} = 250 nm).

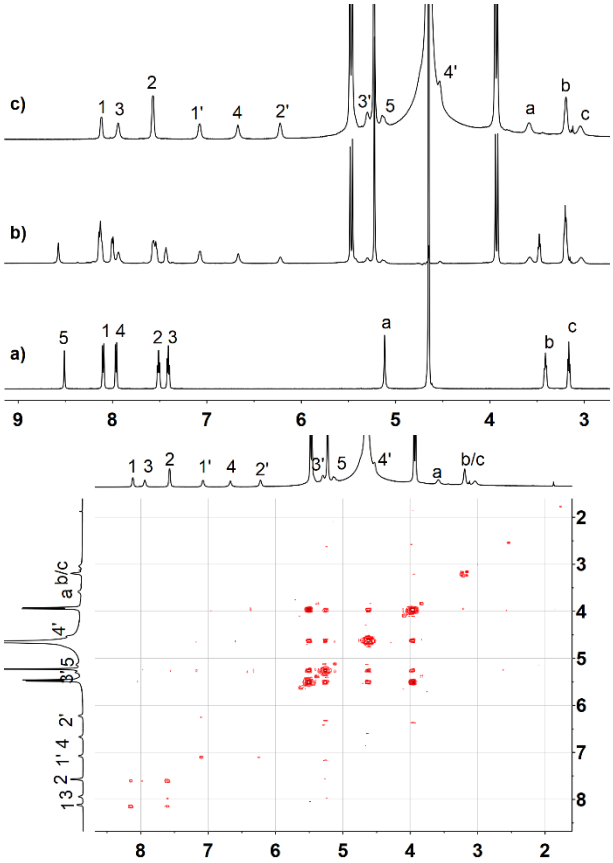


Fig. S9 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of a) free **G2** (2.5 mM), b) 4:1 mixture of **G2** and CB[8], c) 2:1 mixture of **G2** and CB[8] (top), and partial COSY NMR spectrum of 2:1 mixture of **G2** and CB[8] (bottom).

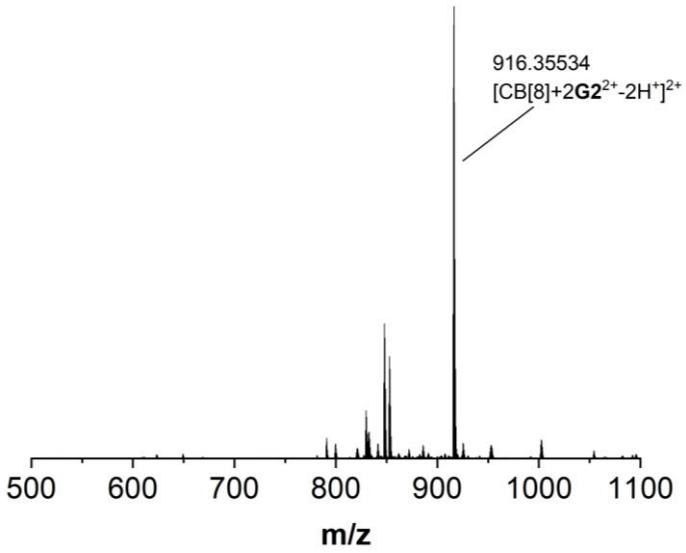


Fig. S10 ESI-MS spectrum of the mixture of **G2** and CB[8].

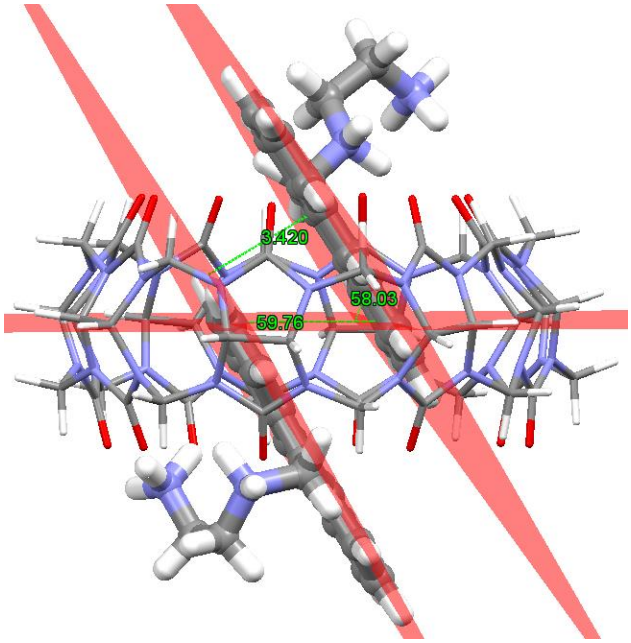


Fig. S11 MMFF-minimized structure of CB[8]·2**G2**.

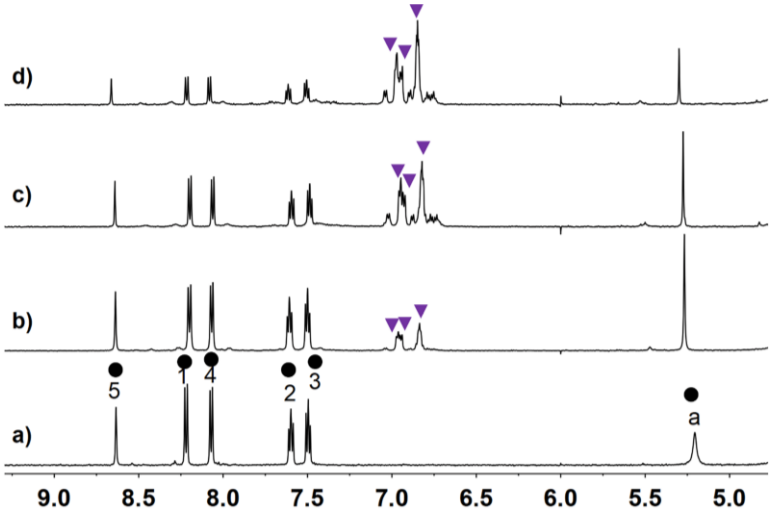


Fig. S12 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) **G2** (2.5 mM); b) **G2** after UV irradiation for 1 h; c) **G2** after UV irradiation for 3 h; d) **G2** after UV irradiation for 6 h (resonances of **G2** are marked with '●'; resonances of **DG2** (head-to-tail) are marked with '▼').

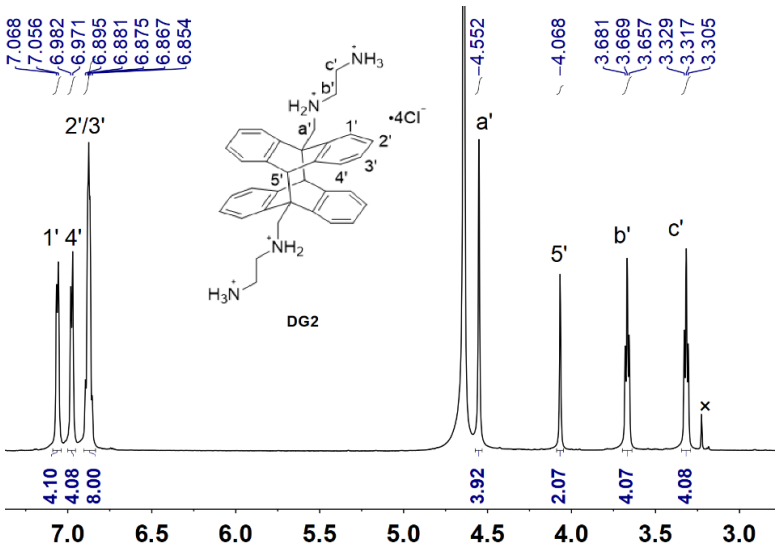


Fig. S13 ^{1}H NMR spectrum (600 MHz, D_2O, 298 K) of photoreaction product (**DG2**). δ (ppm) 7.07 – 6.85 (m, 16H), 4.55 (s, 4H), 4.07 (s, 2H), 3.59 (t, J = 7.1 Hz, 4H), 3.23 (t, J = 7.1 Hz, 4H) (proton signal of impurity is marked with '×').

(work-up procedure: the aqueous solution of CB[10]·2**G2** after UV irradiation for sufficient time was added appropriate amount of 3,5-dimethylamantadine hydrochloride (3,5-DMADA) and sonicated. The resulted precipitate (CB[10]·2(3,5-DMADA)) was removed by centrifuge. The clear aqueous solution was evaporated and the residue was dried at high vacuum to give **DG2**)

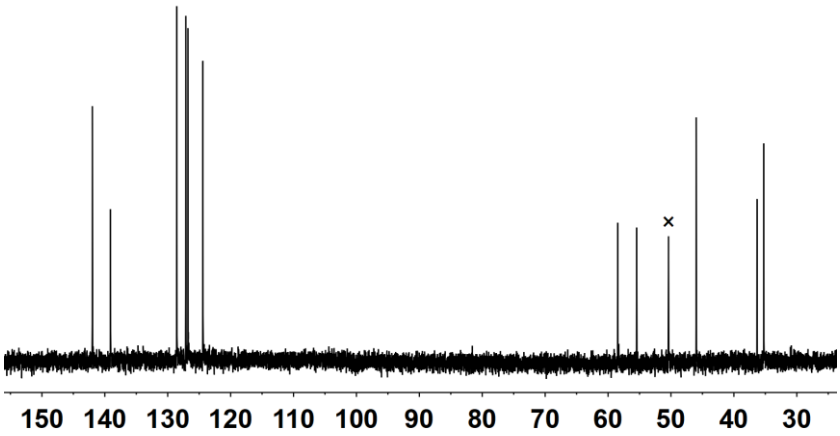


Fig. S14 ^{13}C NMR spectrum (150 MHz, D_2O, 298 K) of dimerization product **DG2** (δ 141.98, 139.10, 128.57, 127.13, 126.80, 124.41, 58.46, 55.46, 46.00, 36.32, 35.25, carbon signal of CH_3OH is marked with '×').

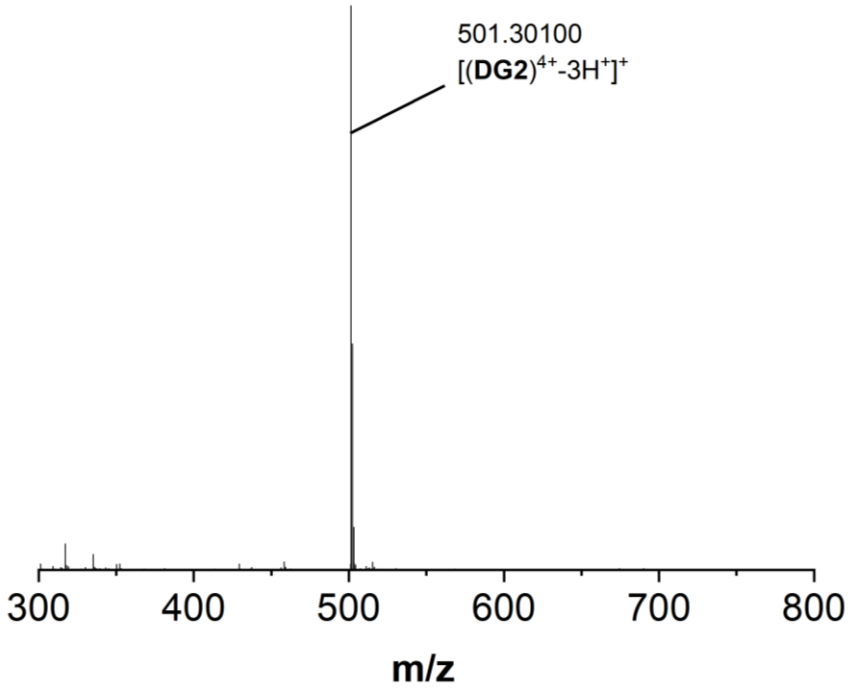


Fig. S15 ESI-MS spectrum of **DG2**.

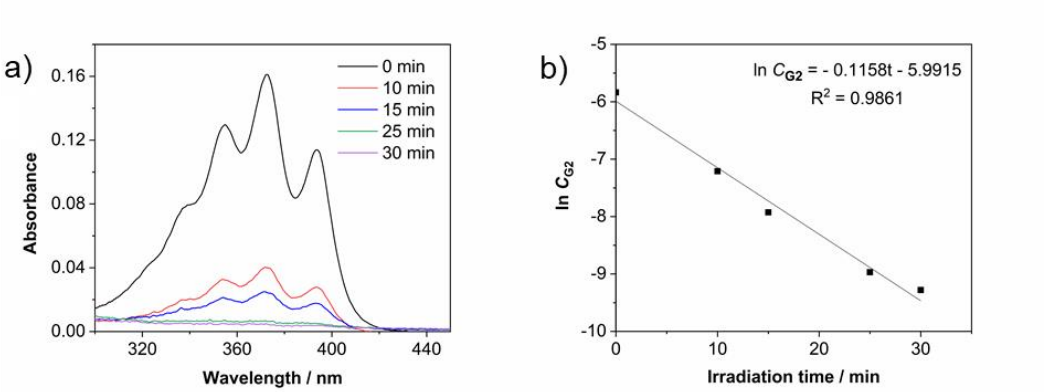


Fig. S16 a) UV/Vis spectral changes upon photodimerization of **G2** in the presence of CB[10] (0.5 equiv.) at rt in water. b) First-order kinetics plot affording k_1 as 0.1158 ± 0.0079 min^{-1} (by monitoring absorbance changes at λ = 370 nm). After irradiation, 2.5 mM of **G2** with CB[10] was diluted to 31.25 µM for UV/Vis measurement.

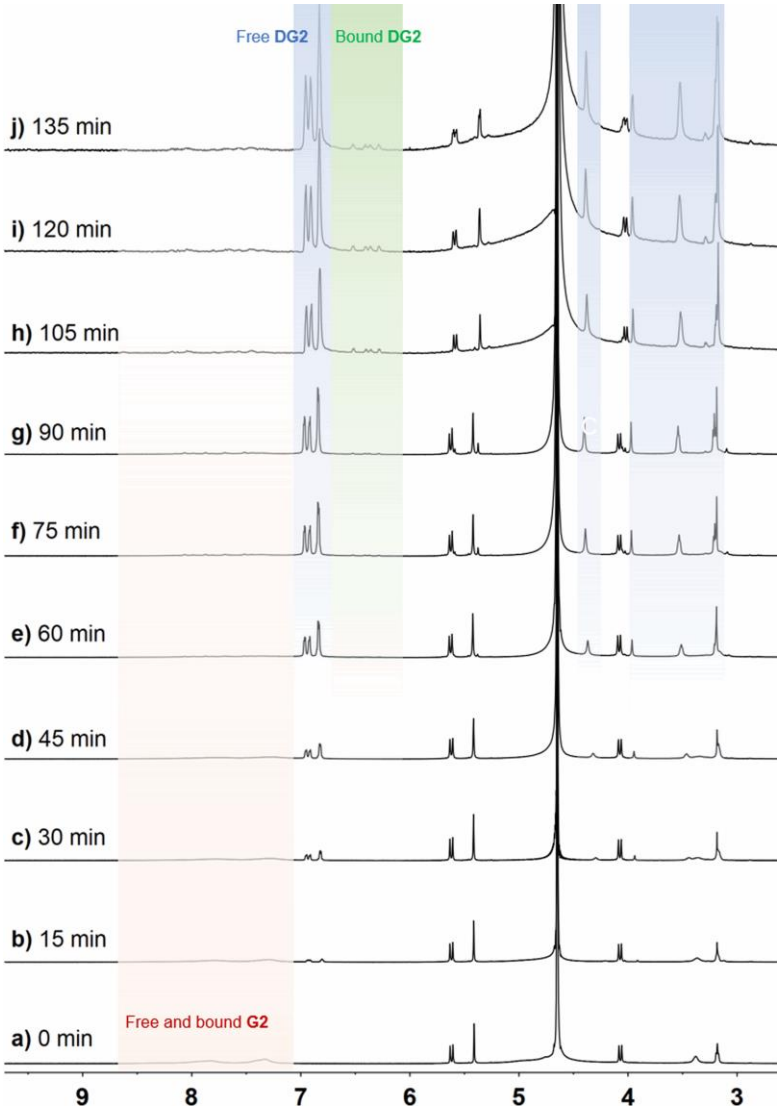
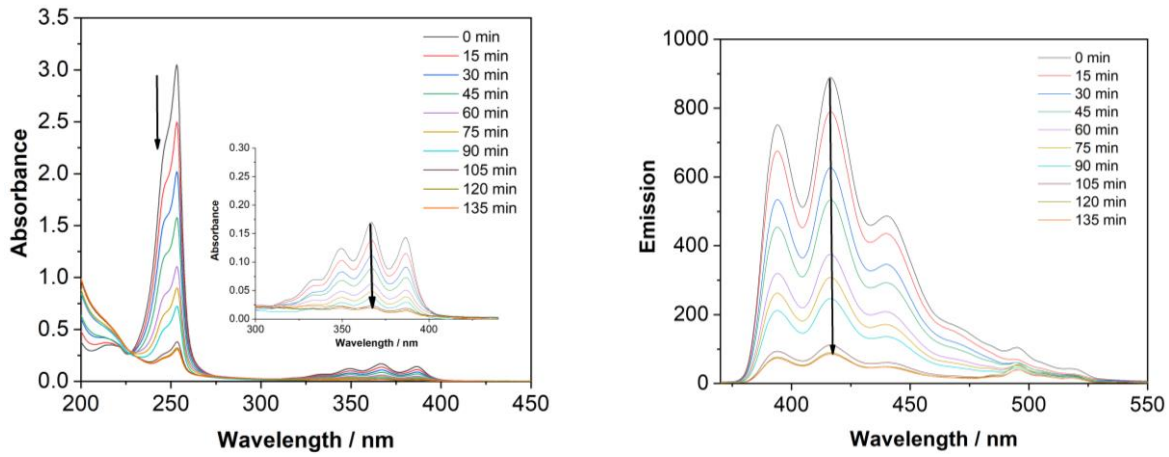


Fig. S17 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of **G2** solution (2.5 mM) containing CB[10] (0.1 equiv., 10%) with various irradiation time (peaks of free **DG2** are marked in blue area; peaks of bound **DG2** are marked in green area; peaks of **G2** are marked in red area).



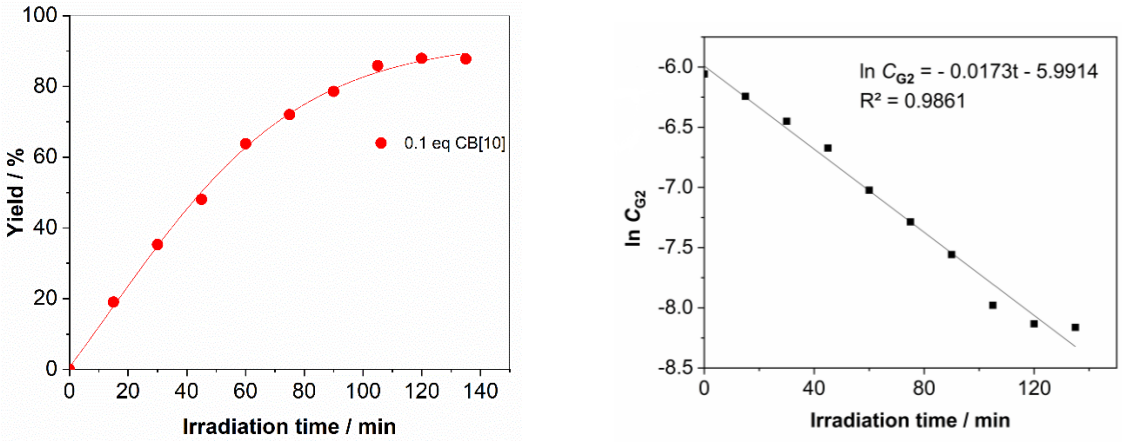


Fig. S18 UV/Vis and fluorescence emission (λ_{ex} = 250 nm) spectral changes upon photodimerization of **G2** in the presence of CB[10] (0.1 equiv.) at rt in water (top left & right), diagram of the yield of **DG2** *VS* irradiation time (by monitoring absorbance changes at λ = 370 nm) (bottom left), and the first-order kinetics plot affording k_1 as 0.0173 ± 0.0007 min^{-1} (bottom right). After irradiation, 2.5 mM of **G2** with CB[10] was diluted to 31.25 μM for UV/Vis and fluorescence emission measurement.

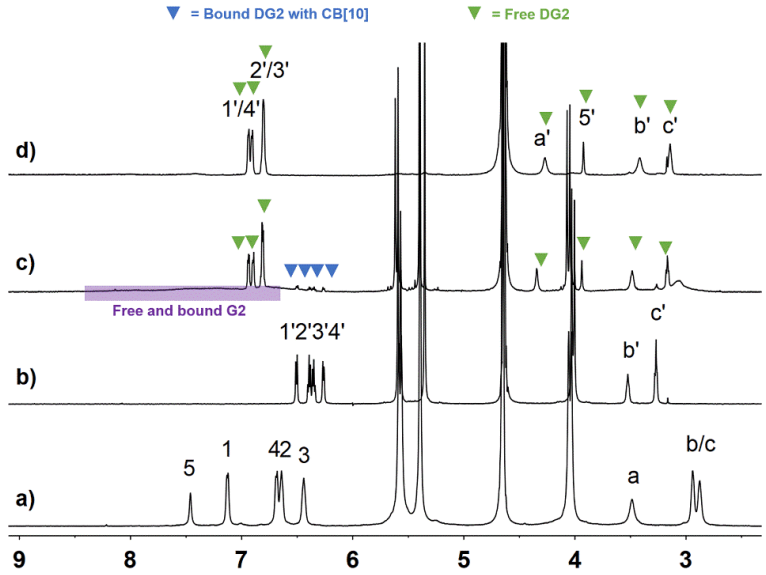


Fig. S19 ^{1}H NMR spectra for the competition binding between **G2** and **DG2** with CB[10] (600 MHz, D_2O, 298 K): a) 2:1 mixture of **G2** (2.5 mM) with CB[10]; b) 1:1 mixture of **DG2** (1.25 mM) with CB[10]; c) 2:1:1 mixture of **G2** (2.5 mM), **DG2** and CB[10]; d) free **DG2**.

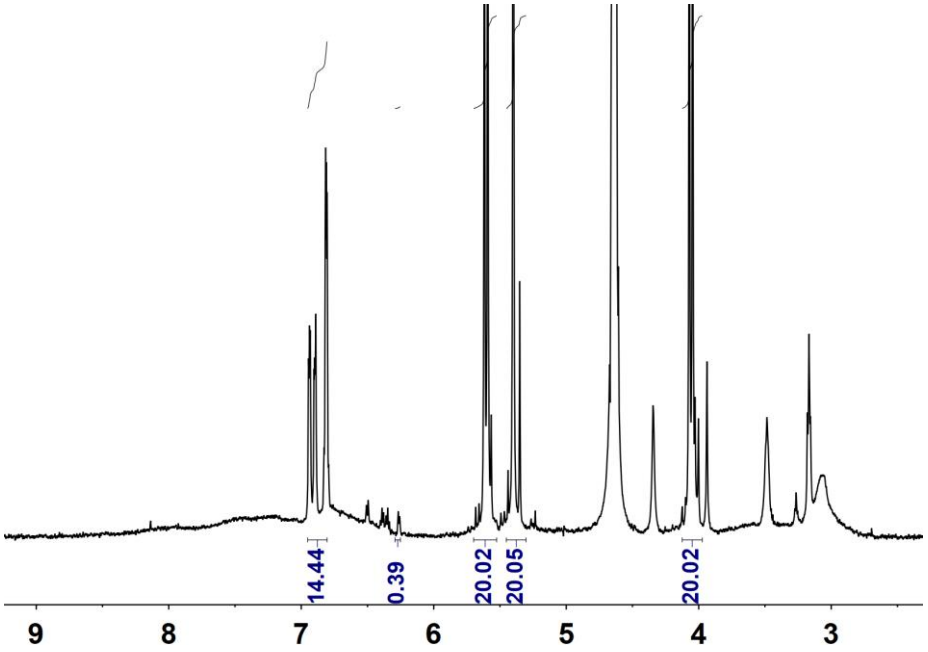


Fig. S20 ^{1}H NMR spectrum of 2:1:1 mixture of **G2** (2.5 mM), **DG2** and CB[10] (600 MHz, D_2O, 298 K). Integrals were used to calculate the concentrations of all species in the solution.

$$2\mathbf{G2} + \text{CB[10]}\cdot\mathbf{DG2} \rightleftharpoons \text{CB[10]}\cdot 2\mathbf{G2} + \mathbf{DG2}$$

$$K_{eq} = \frac{[\text{CB[10]}\cdot 2\mathbf{G2}]\times[\mathbf{DG2}]}{[\text{CB[10]}\cdot\mathbf{DG2}]\times[\mathbf{G2}]^2}$$

$$= 8.8 \times 10^5\ \text{M}^{-1}$$

Fig. S21 The calculation on the equilibrium constant (K_{eq}) of the competitive host-guest complexation.

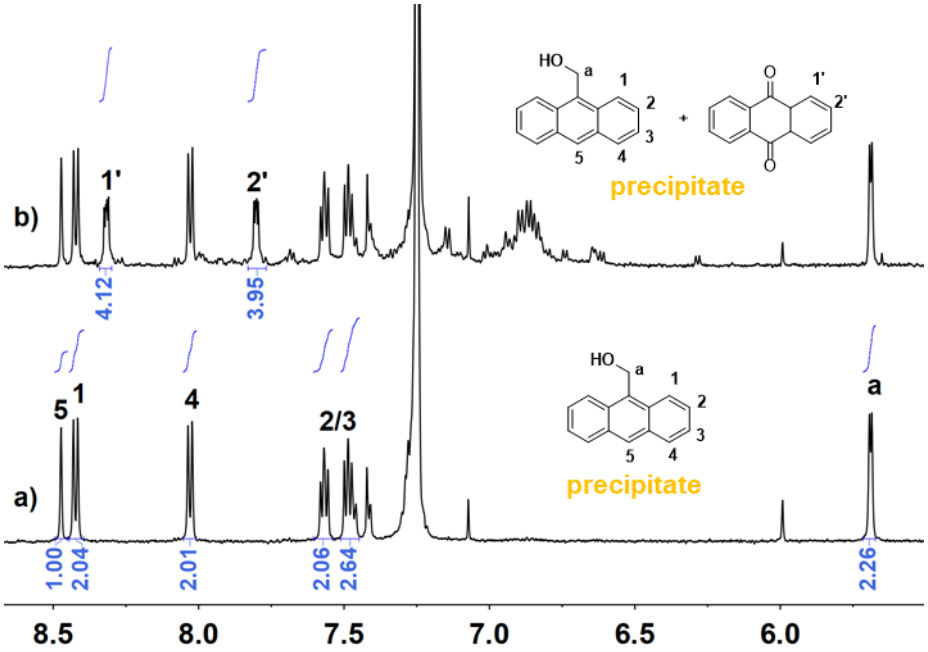


Fig. S22 ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of: a) the yellow precipitate formed by UV irradiating 2:1 mixture of **G2** (2.5 mM) and CB[8] (photoreaction was carried out at N_2 atmosphere); b) the yellow precipitate formed by UV irradiating 2:1 mixture of **G2** (2.5 mM) and CB[8] for 1 hour in air.

(isolation of the yellow precipitate: after irradiating the aqueous solution of CB[8]·2**G2** , the resulted yellow precipitate was centrifuged and dried to give 9-anthracenemethanol with almost quantitative yield)

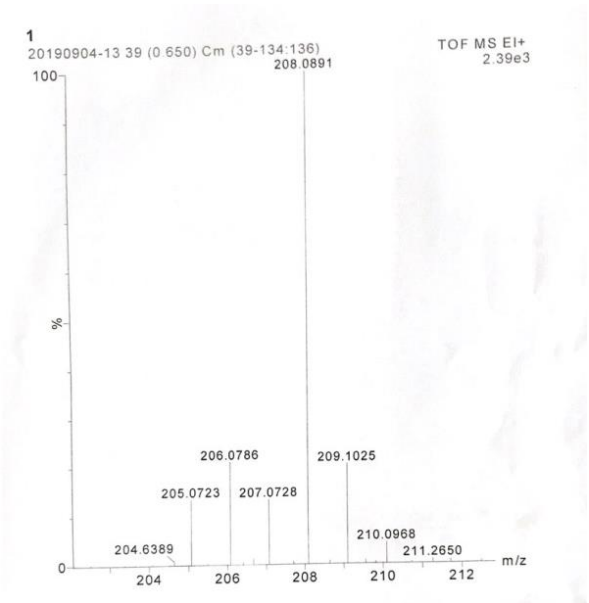


Fig. S23 EI spectrum of the yellow precipitate (calculated for 9-anthracenemethanol: 208.09).

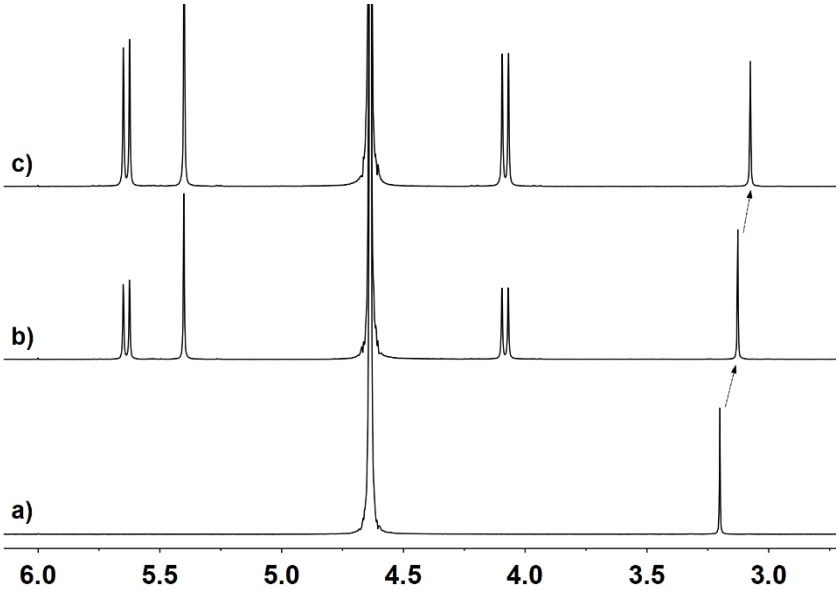


Fig. S24 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) free 2.5 mM ethylenediamine (**EDA**) dihydrochloride; b) 4:1 mixture of **EDA**·2HCl and CB[8]; c) 2:1 mixture of **EDA**·2HCl and CB[8].

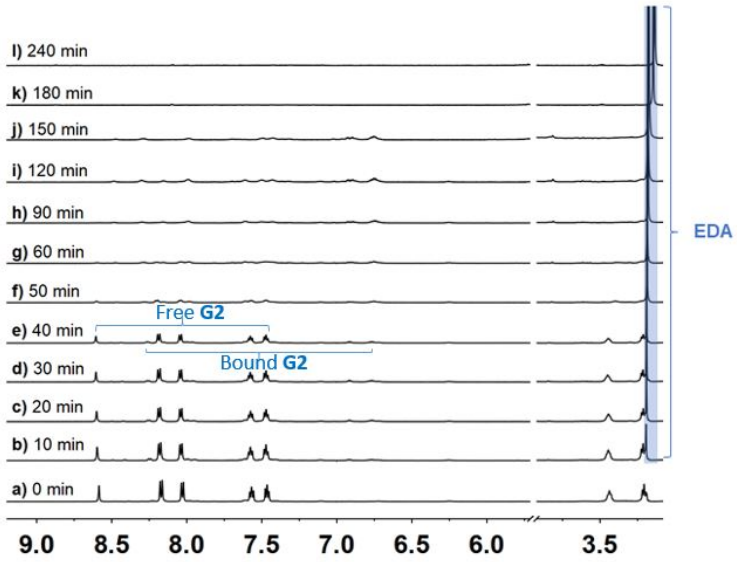


Fig. S25 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of **G2** solution (2.5 mM) containing CB[8] (0.05 equiv., 5%) with various irradiation time (after irradiation, all samples were centrifuged before checked by NMR).

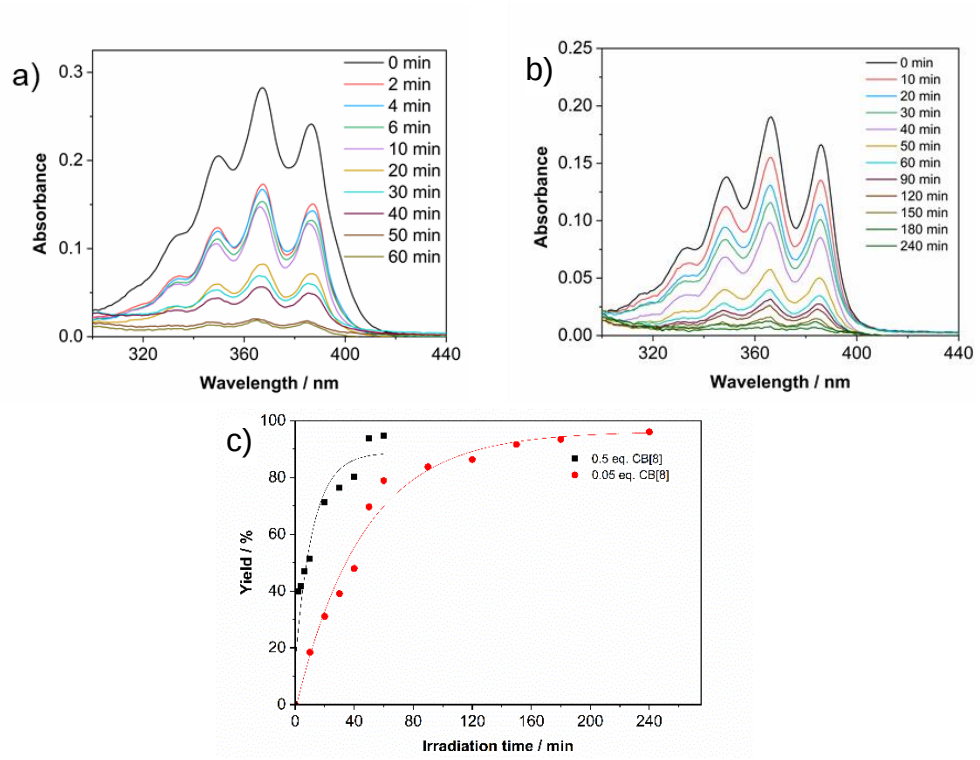


Fig. S26 UV/Vis spectral changes upon photosolvolysis of **G2** in the presence of a) 0.5 equiv. and b) 0.05 equiv. of CB[8]. c) Diagram of the yield of 9-anthracenemethanol *VS* irradiation time (by monitoring absorbance changes at λ = 370 nm). After irradiation, 2.5 mM of **G2** with CB[8] solution was centrifuged then the solution was diluted to 31.25 µM for UV/Vis measurement.

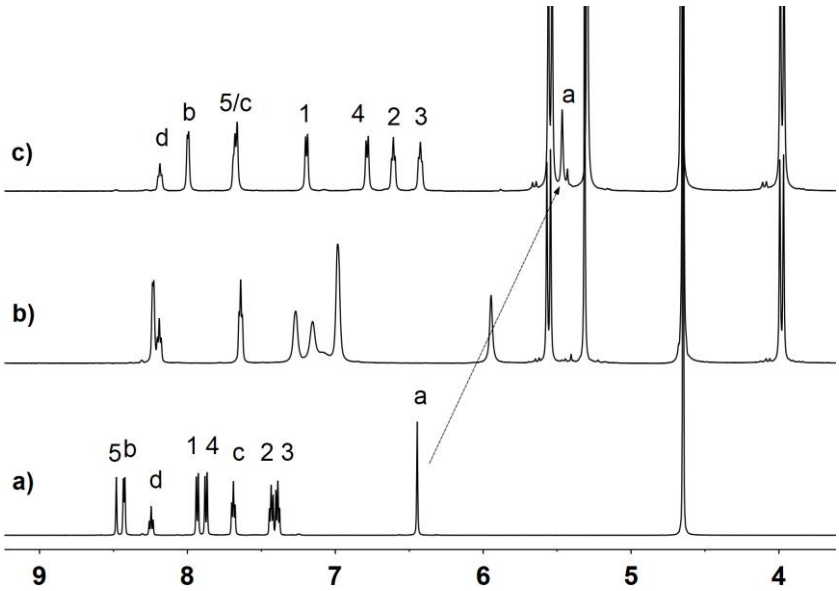


Fig. S27 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of a) free **G3** (2.5 mM), b) 4:1 mixture of **G3** and CB[10], and c) **G3** and excess CB[10].

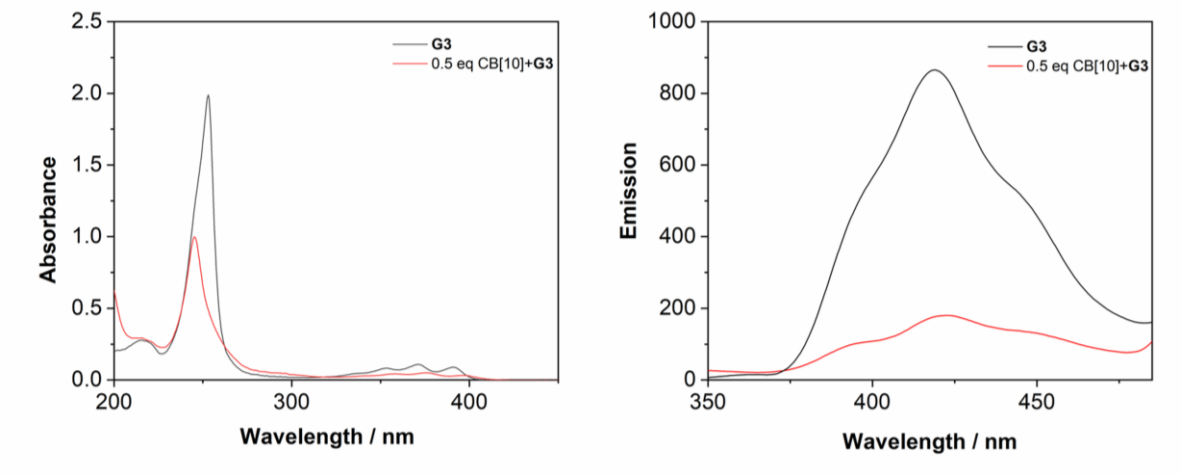


Fig. S28 UV/Vis spectra of **G3** (15.63 µM) and fluorescence emission spectra **G3** (31.25 µM) with addition of CB[10] (0.5 equiv.) (λ_{ex} = 250 nm).

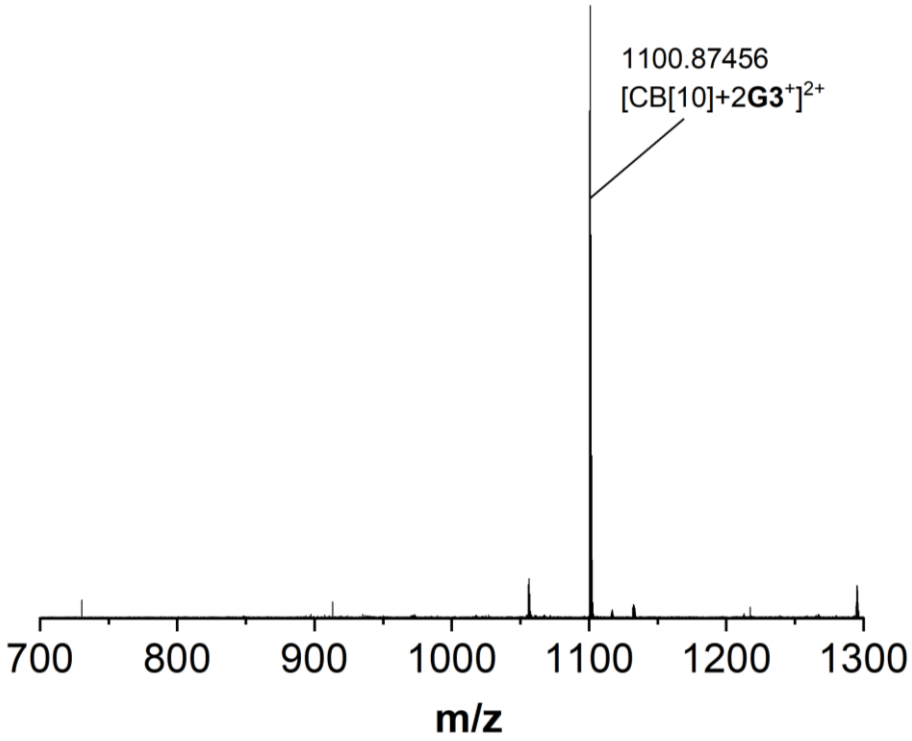


Fig. S29 ESI-MS spectrum of **G3** with excess CB[10].

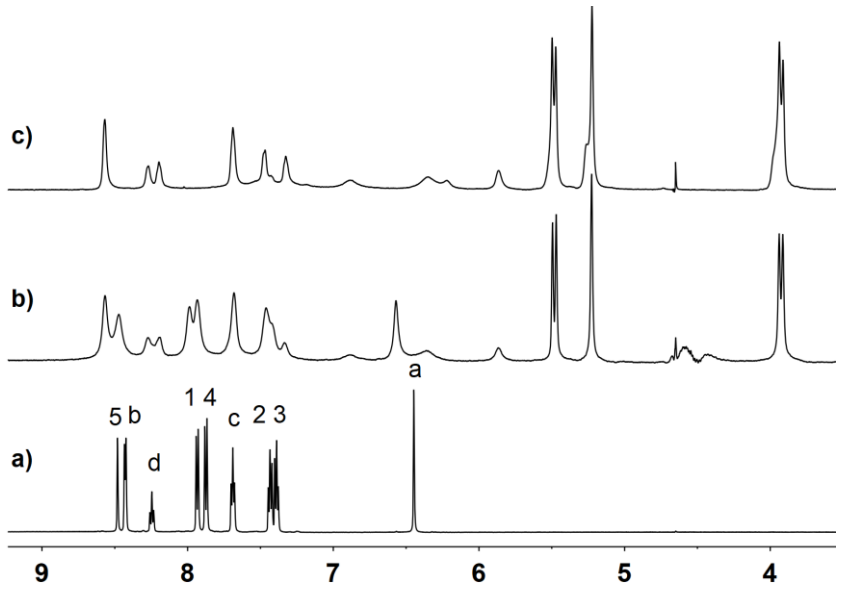


Fig. S30 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of a) free **G3** (2.5 mM), b) 4:1 mixture of **G3** and CB[8], and c) 2:1 mixture of **G3** and CB[8].

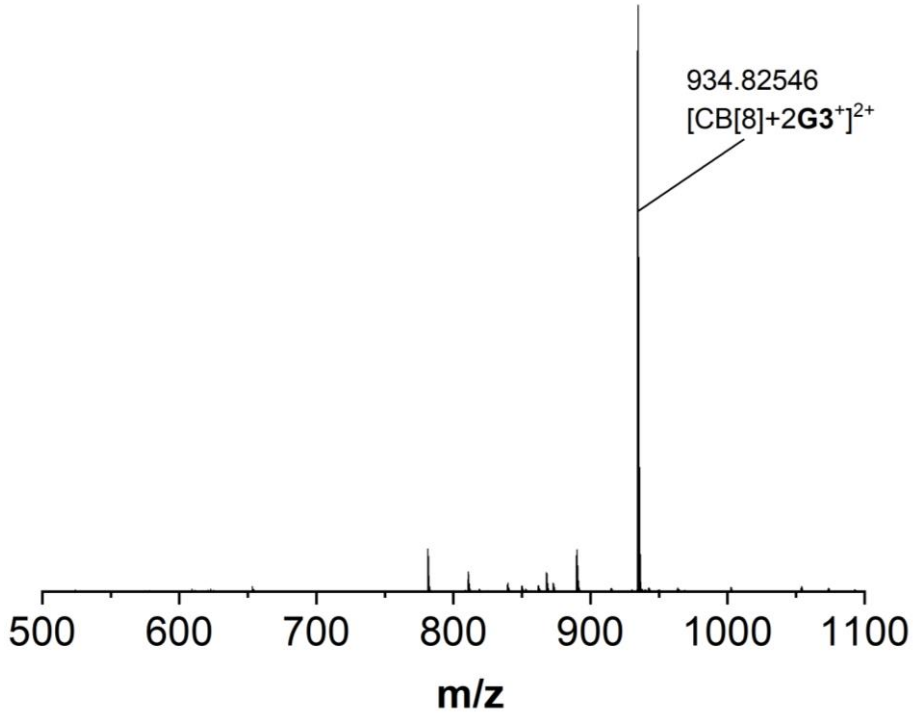


Fig. S31 ESI-MS spectrum of the mixture of **G3** and CB[8].

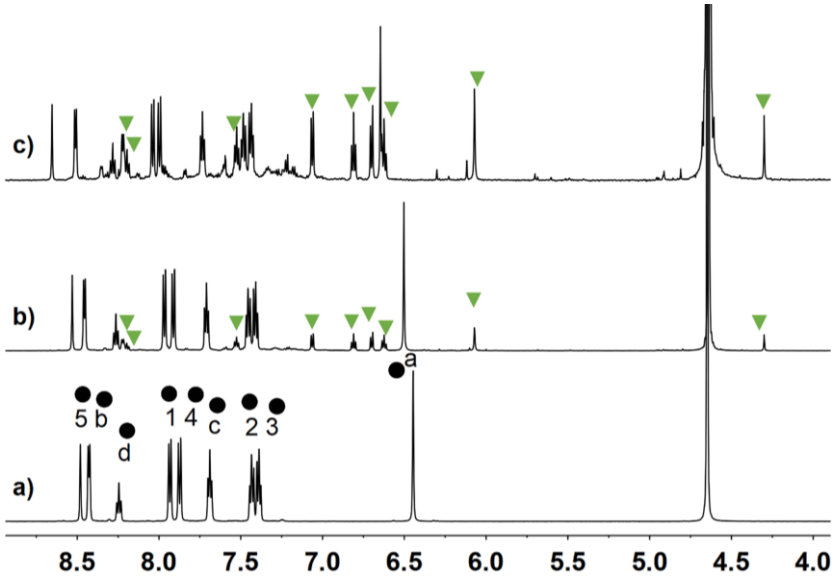


Fig. S32 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) **G3** (2.5 mM); b) **G3** after UV irradiation for 3 hours; c) **G3** after UV irradiation for 8 hours; (resonances of **G3** are marked with '●'; resonances of **DG3** (head-to-tail) are marked with '▼').

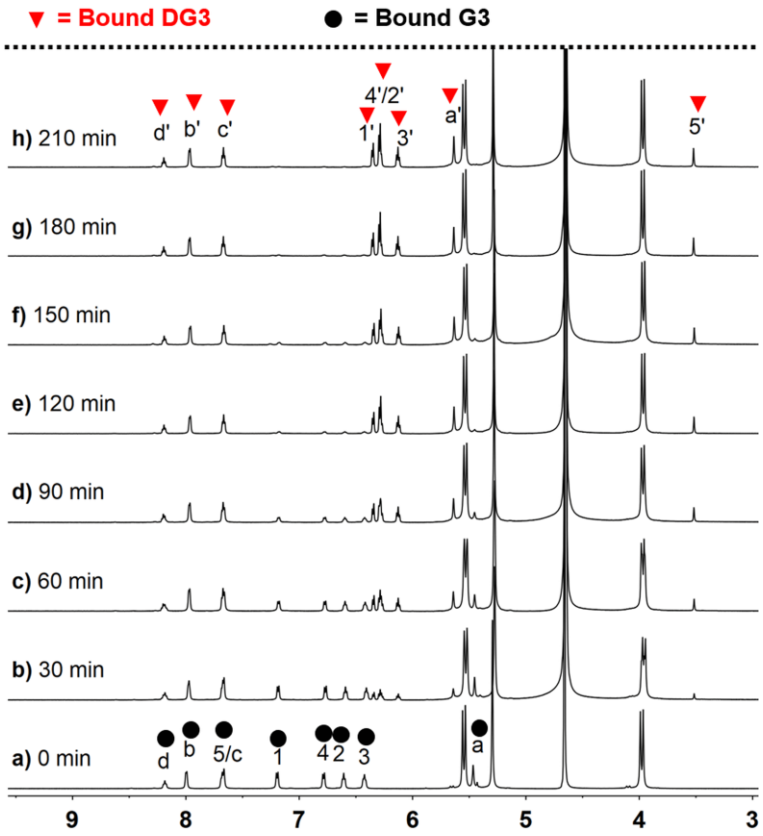


Fig. S33 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of CB[10]·2**G3** ([**G3**] = 2.5 mM) solution with various UV irradiation time.

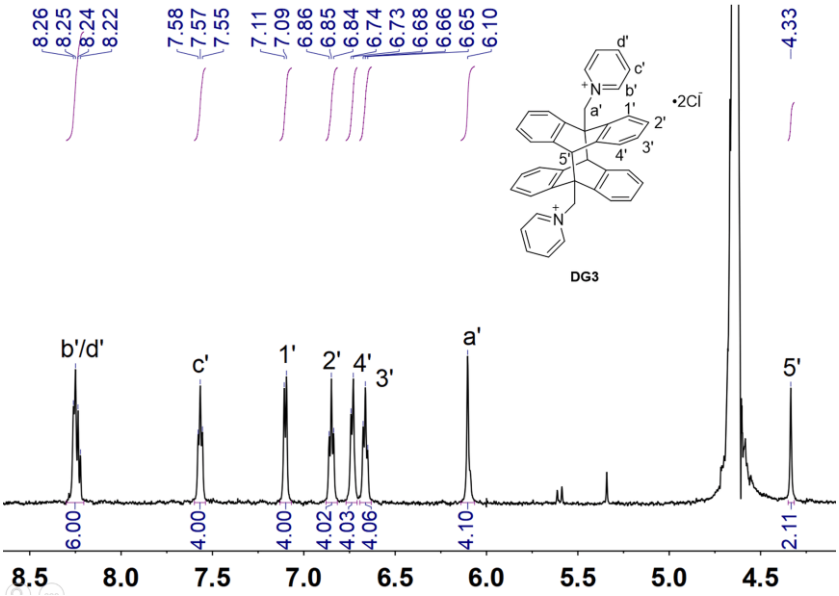


Fig. S34 ^{1}H NMR spectrum (600 MHz, D_2O, 298 K) of photoreaction product (**DG3**). δ (ppm) 8.30 – 8.20 (m, 6H), 7.57 (t, J = 7.1 Hz, 4H), 7.10 (d, J = 7.5 Hz, 4H), 6.85 (t, J = 7.4 Hz, 4H), 6.74 (d, J = 7.7 Hz, 4H), 6.66 (t, J = 7.6 Hz, 4H), 6.10 (s, 4H), 4.33 (s, 2H). **DG3** was isolated according to the same procedure for **DG2** (Fig. S12).

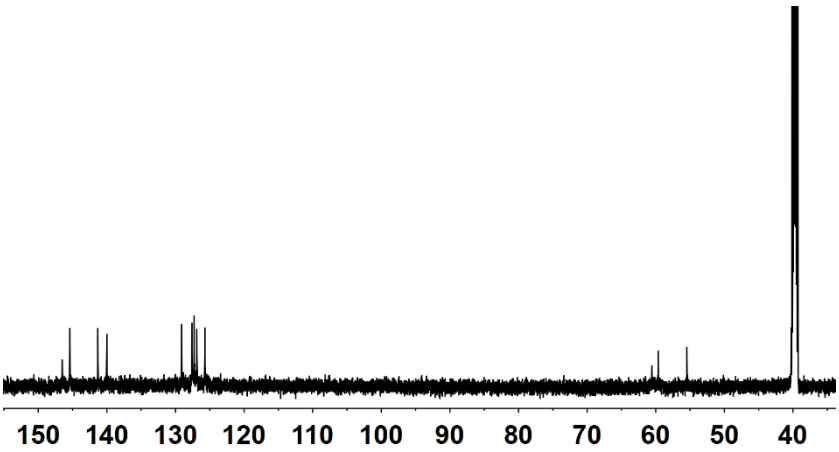


Fig. S35 ^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of **DG3**. δ (ppm) 146.51, 145.38, 141.30, 139.99, 129.10, 127.58, 127.27, 126.87, 125.71, 60.57, 59.61, 55.45.

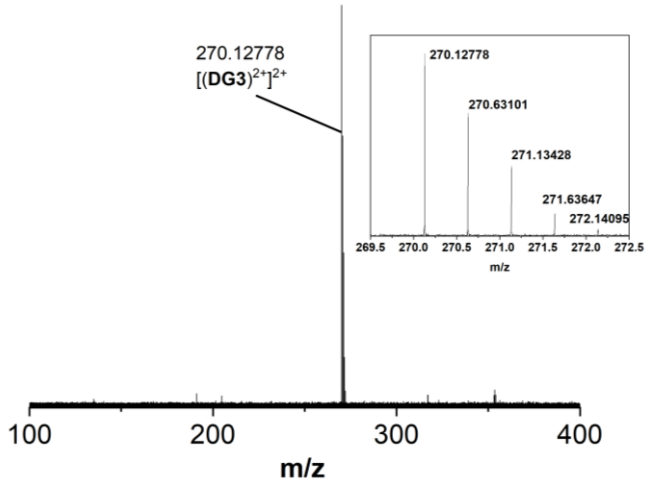


Fig. S36 ESI-MS spectrum of **DG3**.

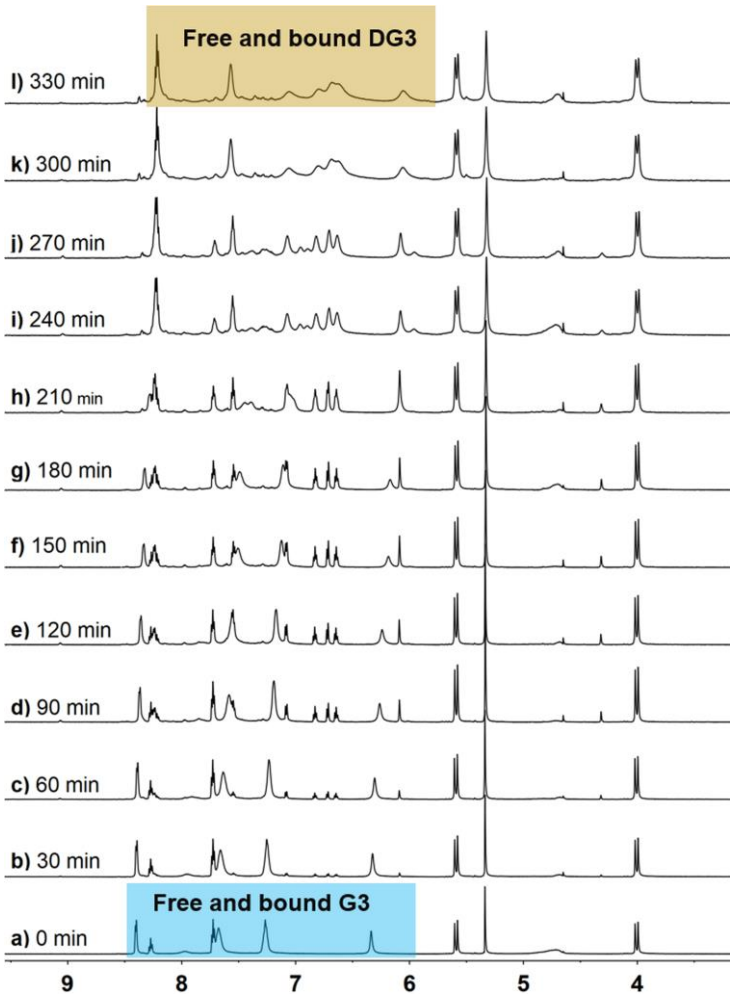


Fig. S37 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of **G3** solution (2.5 mM) containing CB[10] (0.1 equiv., 10%) with various irradiation time.

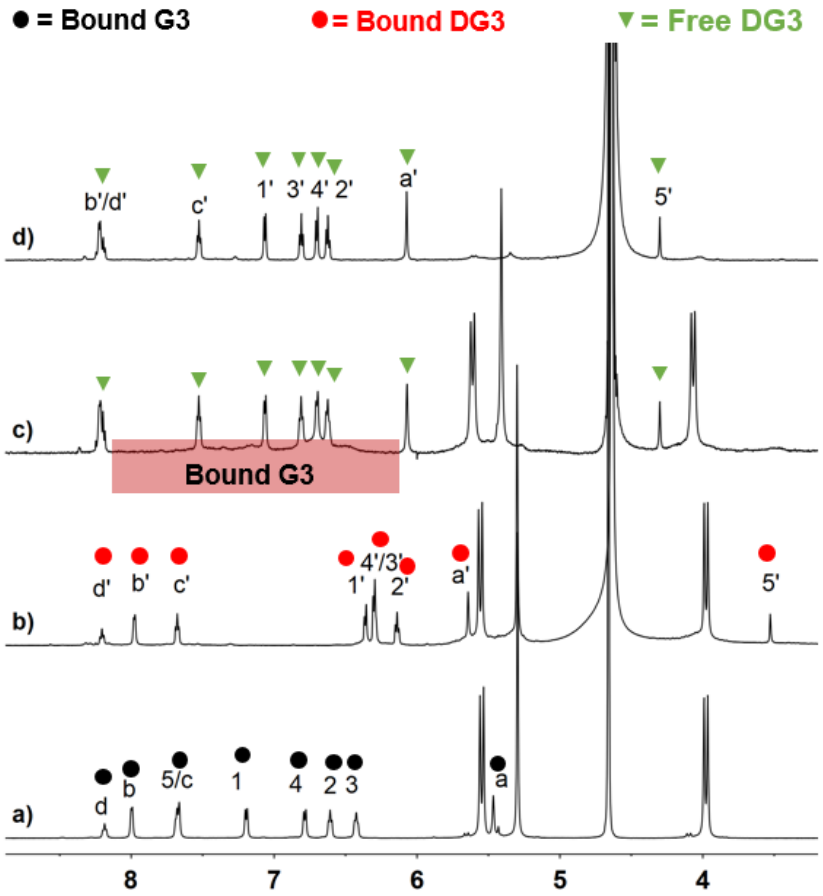
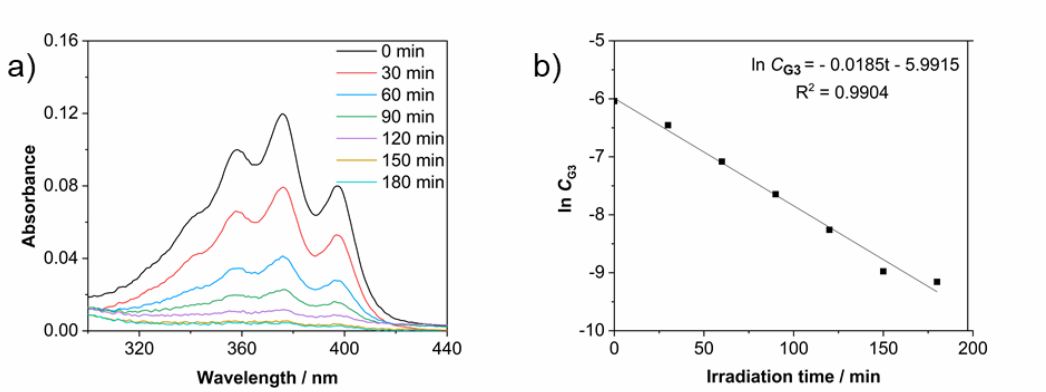


Fig. S38 ^{1}H NMR spectra for the competition binding between **G3** and **DG3** with CB[10] (600 MHz, D_2O, 298 K): a) 2:1 mixture of **G3** (2.5 mM) with CB[10]; b) 1:1 mixture of **DG3** (1.25 mM) with CB[10]; c) 2:1:1 mixture of **G3** (2.5 mM), **DG3**, and CB[10]; d) free **DG3**.



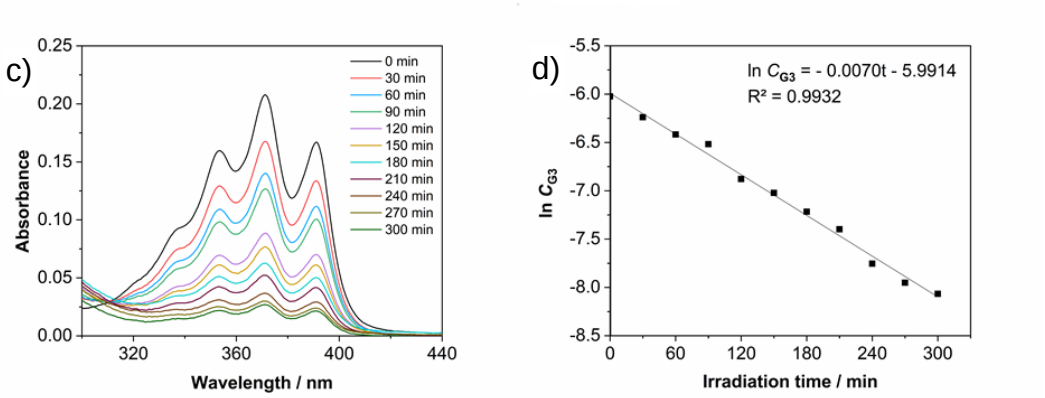


Fig. S39 a) UV/Vis spectral changes upon photodimerization of **G3** in the presence of CB[10] (0.5 equiv.) at rt in water. b) First-order kinetics plot affording k_1 as 0.0185 ± 0.0008 min^{-1}. c) UV/Vis spectral changes upon photodimerization of **G3** in the presence of CB[10] (0.1 equiv.). d) First-order kinetics plot affording k_1 as 0.0070 ± 0.0002 min^{-1}. After irradiation, 2.5 mM of **G3** with CB[10] was diluted to 31.25 µM for UV/Vis measurement.

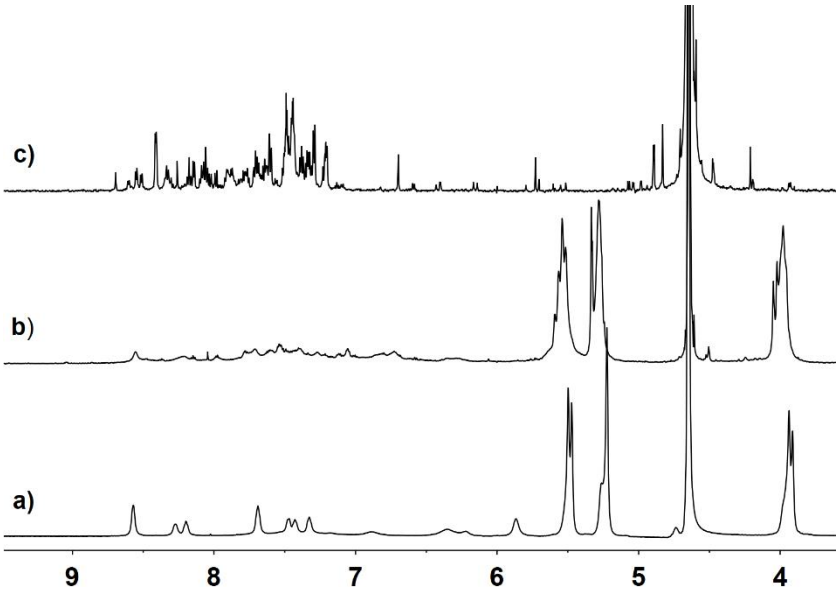


Fig. S40 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of: a) 2:1 mixture of **G3** (2.5 mM) and CB[8]; b) 2:1 mixture of **G3** and CB[8] after irradiation for 8 hours; c) photoproducts of **G3** in the presence of 0.5 equiv. of CB[8] (CB[8] was removed by adding appropriate amount of 3,5-dimethylamantadine hydrochloride to the solution, followed by precipitating the complex).