

Supporting Information

A supramolecular strategy for gated photochromism in aqueous solution and solid state

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Table of Contents	Page
Table of Contents	S1
General Experimental Section	S2
Synthesis and characterization of Go	S3-S6
Host-guest recognition	S7
Photoreaction of G	S8
Crystal data of CB[10]· Go	S9-S10
PXRD pattern of CB[10]· Go	S11

General Experimental Section

ESI-MS measurements: ESI-MS were performed on a Solarix 9.4T.

UV/Vis measurements: The experiments were performed on a SHIMADZU UV-36002 instrument at 298 K.

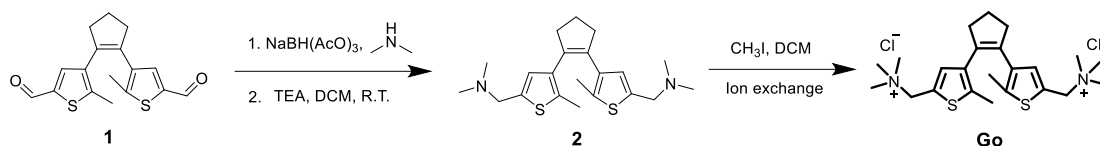
¹H NMR measurements: All ¹H and ¹³C NMR spectra were collected on Agilent 600 MHz DD2 at 298 K.

Light sources and light Irradiation experiments: The UV light irradiation experiments (in aqueous solution and solid state) were performed using a ZF-7A lamp (the irradiation wavelength for cyclization process is 254 nm, and output power of the lamp is 8 W). The visible light irradiation experiments were carried out with an Hg/Xe lamp (CEL-PF300/T10, visible light output power is 18.6 W) equipped with a cutoff filter (>400 nm, Shenyang HB optical Technology). All the irradiation experiments of aqueous solution were performed in cuvettes directly, which was entirely and evenly exposed in light. Both of **Go** and the host-guest systems were performed in the same solvent, temperature and other conditions.

All the materials were obtained from commercial suppliers and were used without further purification, unless otherwise stated. CB[10] was prepared by the corresponding literature procedures.[1]

Single crystal analysis: A suitable crystal was selected and performed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 200.00 K during data collection. Using Olex2 [2], the structure was solved with the SHELXT [3] structure solution program using Intrinsic Phasing and refined with the SHELXL [4] refinement package using Least Squares minimisation. The corresponding CCDC number (CCDC: 2161361) and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and characterization of G



Scheme S1. Synthesis route of Go

Synthesis of **1** were adapted from previously reported procedures.[5]

Synthesis of 1,1'-(cyclopent-1-ene-1,2-diylbis(5-methylthiophene-4,2-diyl))bis(N,N-dimethylmethanamine) (**2**)

To a mixture of NaBH(OAc)₃ (0.33 g, 1.58 mmol) and compound **1** (0.20 g, 0.63 mmol) in dry DCM (20 mL) was added dimethylamine in THF (1.27 mL, 2 M, 2.53 mmol) and TEA (0.36 mL, 2.53 mmol) under N₂ atmosphere at room temperature. The solution was then stirred for 12 h at room temperature. Afterward, the reaction mixture was poured into water and the resulting mixture was extracted with DCM for three times. The combined organic layers were dried over anhydrous MgSO₄, the solvent was removed in vacuo and the compound **2** was obtained as light yellow oil in 52% yield. ¹H NMR (600 MHz, CDCl₃) δ 6.52 (s, 2H), 3.47 (s, 4H), 2.73 (t, J = 7.4 Hz, 4H), 2.21 (s, 12H), 2.04 – 1.96 (m, 2H), 1.90 (s, 6H), ¹³C NMR (150 MHz, CDCl₃) δ 137.10, 134.96, 134.43, 134.01, 127.25, 58.34, 44.79, 38.24, 23.00, 14.18. ESI-MS: m/z = 375.192353 [M]⁺, calculated exact mass: 375.192317.

Synthesis of 1,1'-(cyclopent-1-ene-1,2-diylbis(5-methylthiophene-4,2-diyl))bis(N,N,N-trimethylmethanaminium) chloride (**Go**)

Compound **2** (0.15 g, 0.65 mmol) was dissolved in dry DCM (10 mL) and CH₃I (0.8 mL) was injected to the solution. The mixture was stirred at room temperature for 24 h. Then acquired white solid and the reaction mixture was filtered, washed with DCM for three times and dried in vacuum to give white solid. The residue was dissolved in MeOH: H₂O (1:1, 20 mL), added excess NH₄PF₆ and the filter cake was filtered, the solid was washed by H₂O for three times in order to wash off excess NH₄PF₆, then dried in vacuum. The obtained solid was dissolved in acetone (10 mL), and excess tetrabutylammonium chloride (TBAC) was added, the filter cake was centrifuged, washed by acetone for three times in order to wash off excess TBAC and dried in vacuum to give white solid **Go** in 82% yield. ¹H NMR (600 MHz, D₂O) δ 7.13 (s, 2H), 4.58 (s, 4H), 3.09 (s, J = 2.3 Hz, 18H), 2.83 (td, J = 7.4, 2.0 Hz, 4H), 2.09 (q, J = 7.6 Hz, 2H), 2.03 (s, J = 2.1 Hz, 6H). ¹³C NMR (150 MHz, D₂O) δ 140.04, 136.56, 135.51, 135.13, 123.88, 63.53, 52.04, 37.61, 22.75, 13.38. ESI-MS: m/z = 202.115482 [M]⁺, calculated exact mass: 202.115447; m/z = 439.200782 [M]²⁺, calculated exact mass: 439.200295.

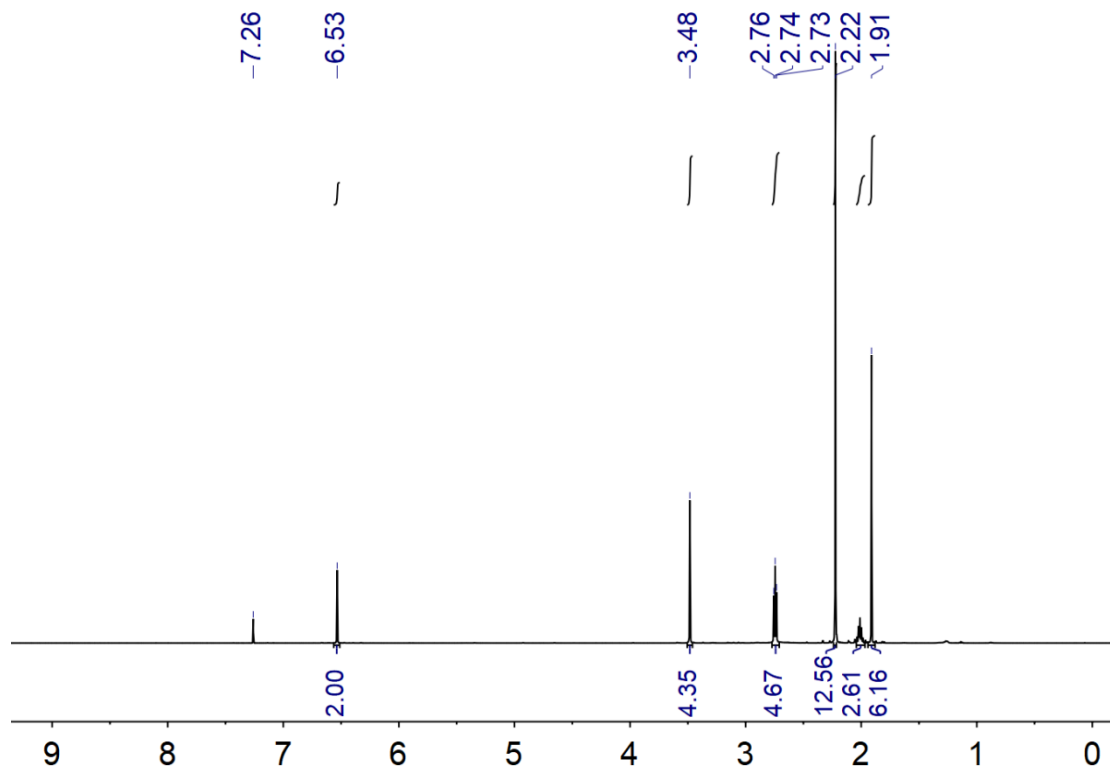


Figure S1. ^1H NMR spectrum recorded for compound **2** (600 MHz, CDCl_3 , 298K).

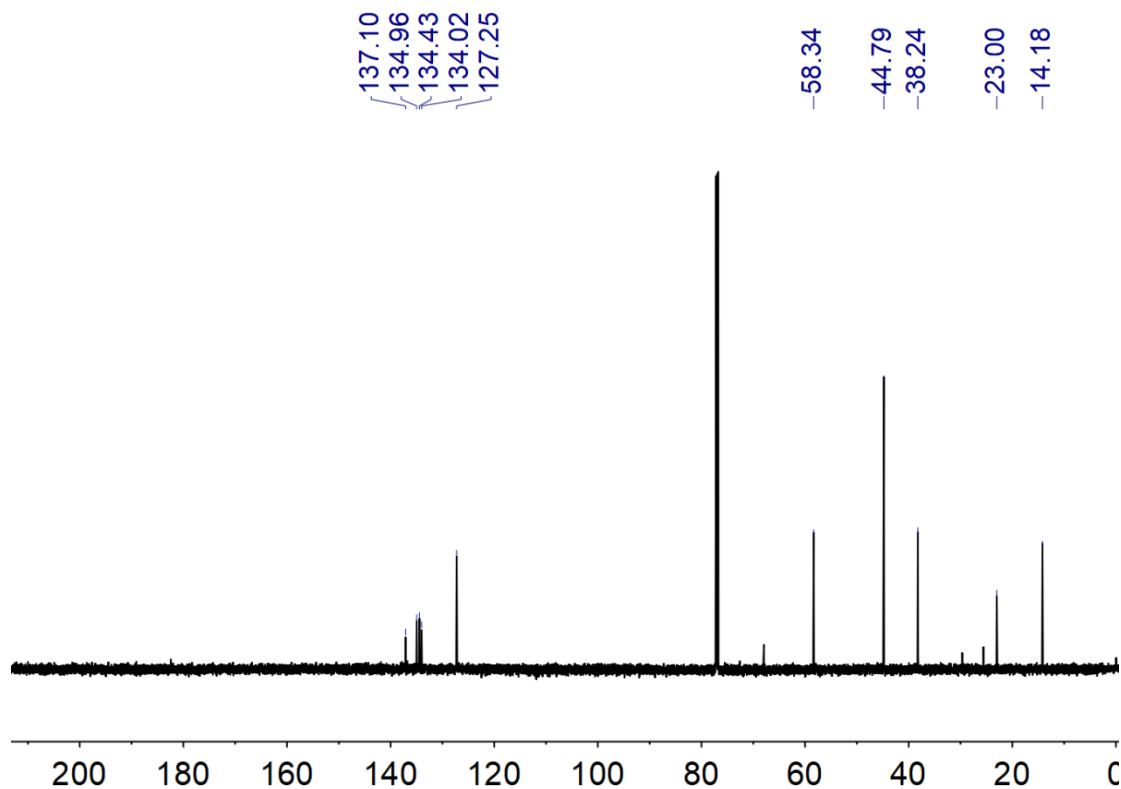


Figure S2. ^{13}C NMR spectrum recorded for compound **2** (150 MHz, CDCl_3 , 298K).

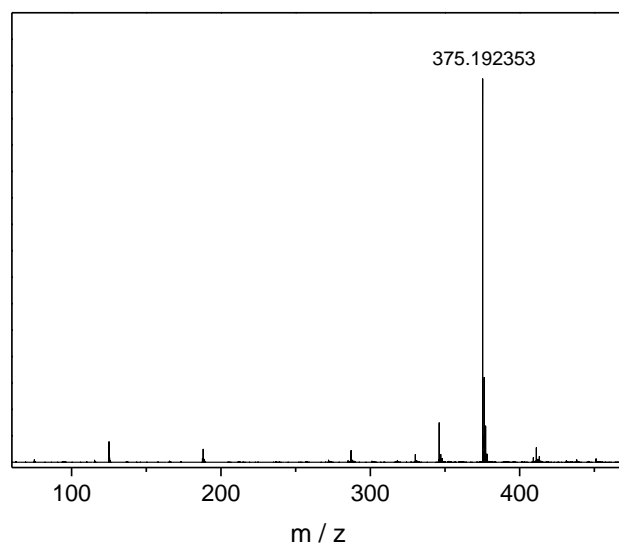


Figure S3. HRMS (ESI) spectrum of compound **2**

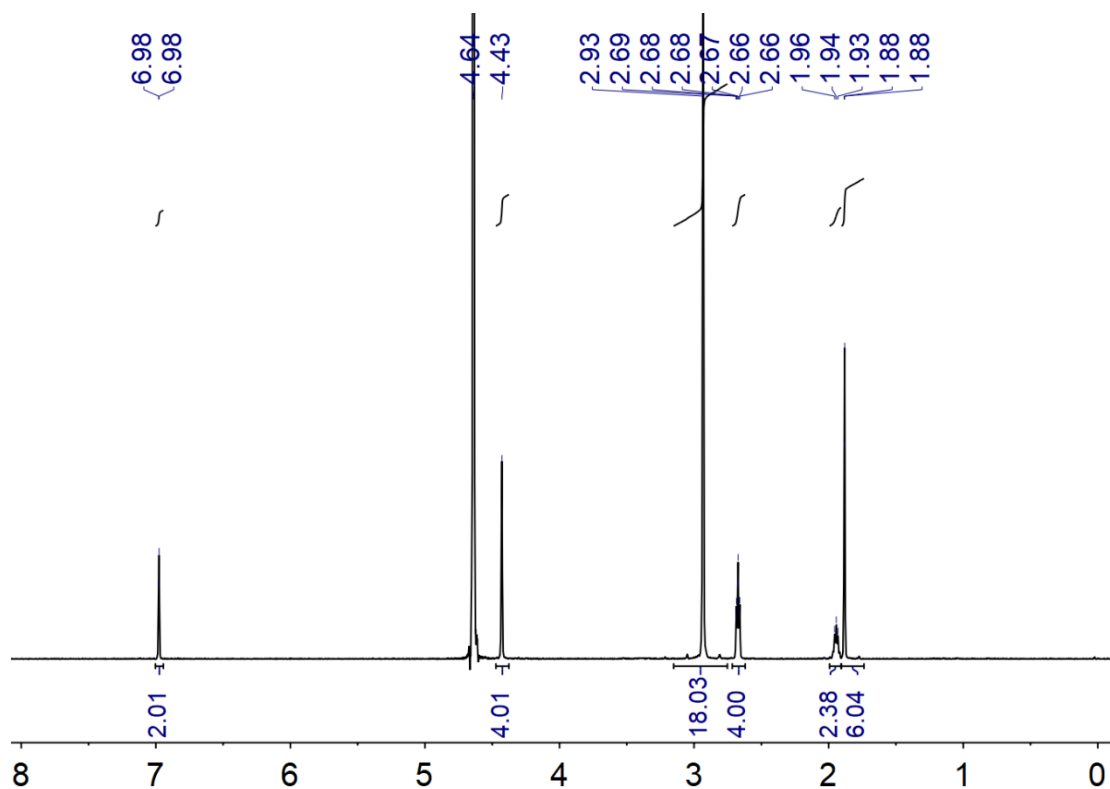


Figure S4. ¹H NMR spectrum recorded for compound **2o** (600 MHz, D₂O, 298K).

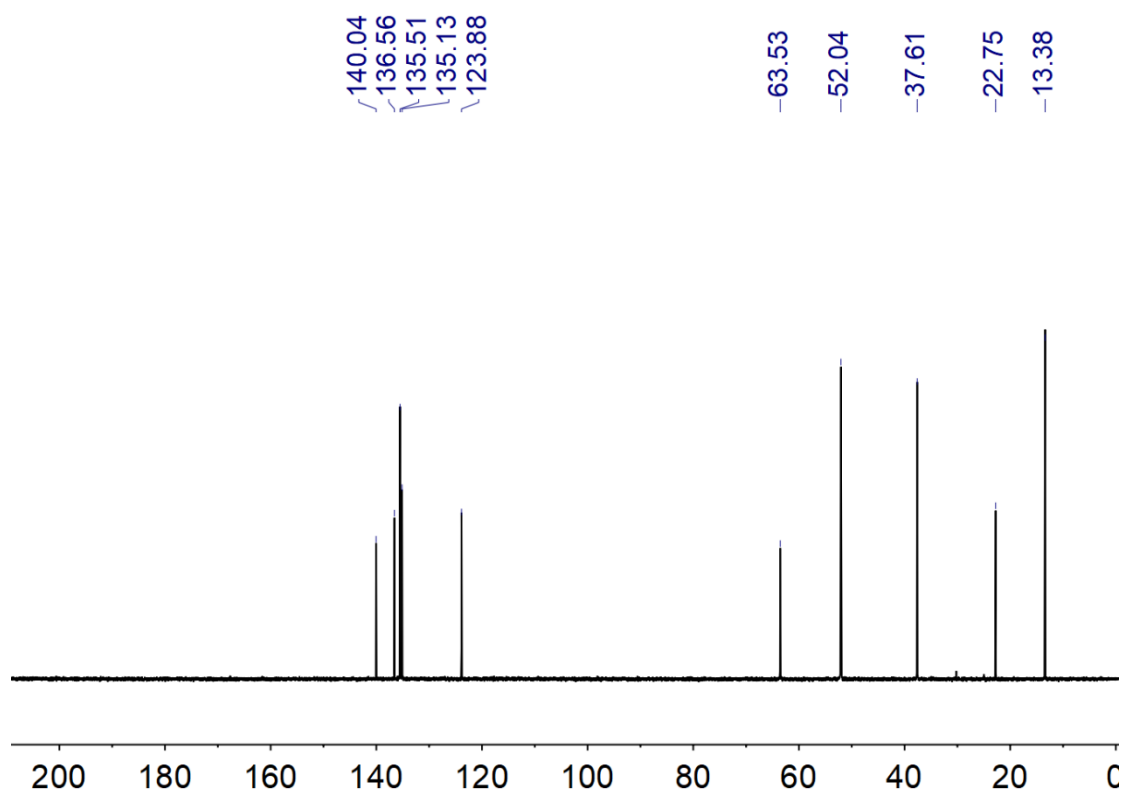


Figure S5. ¹³C NMR spectrum recorded for compound **Go** (150 MHz, D₂O, 298K).

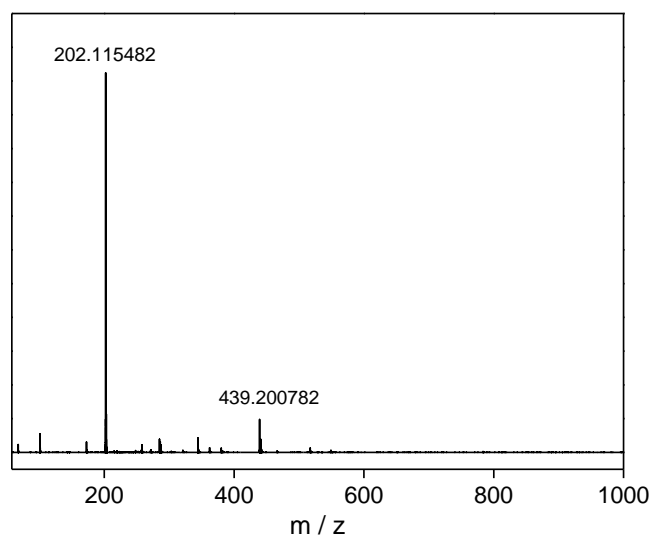


Figure S6. HRMS (ESI) spectrum of compound **Go**

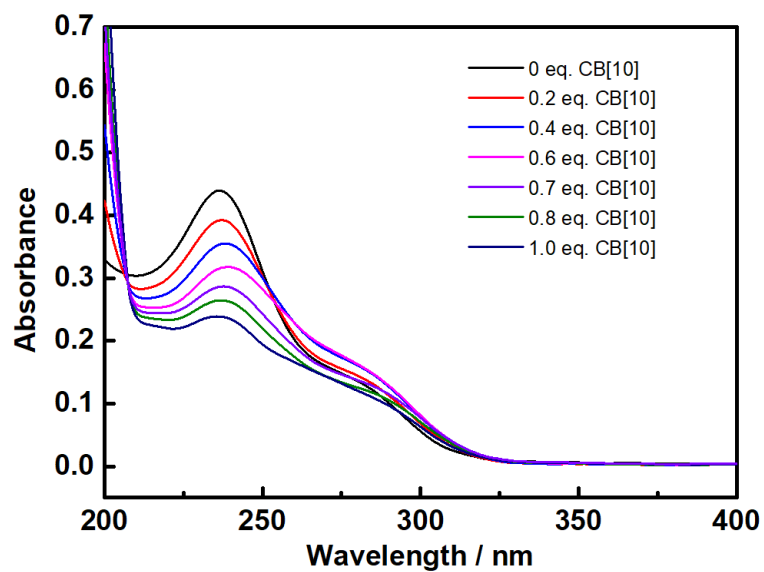


Figure S7. UV-vis absorption spectra of **Go** (20 μM in H₂O) with different equiv. of CB[10].

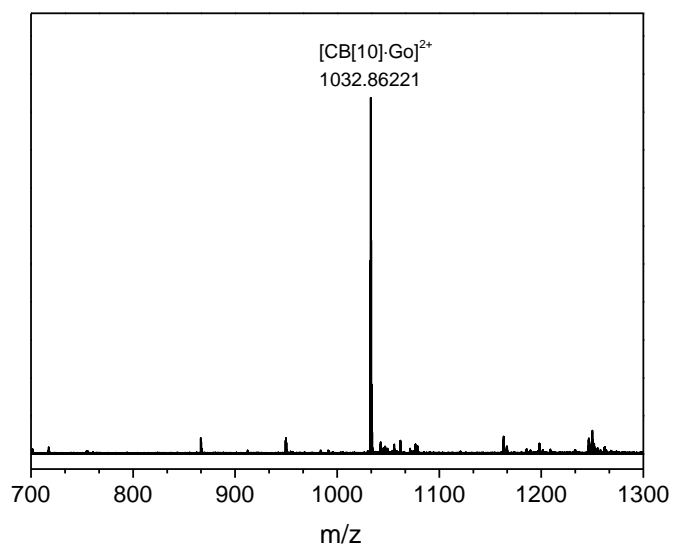


Figure S8. ESI-MS spectrum of CB[10]·Go

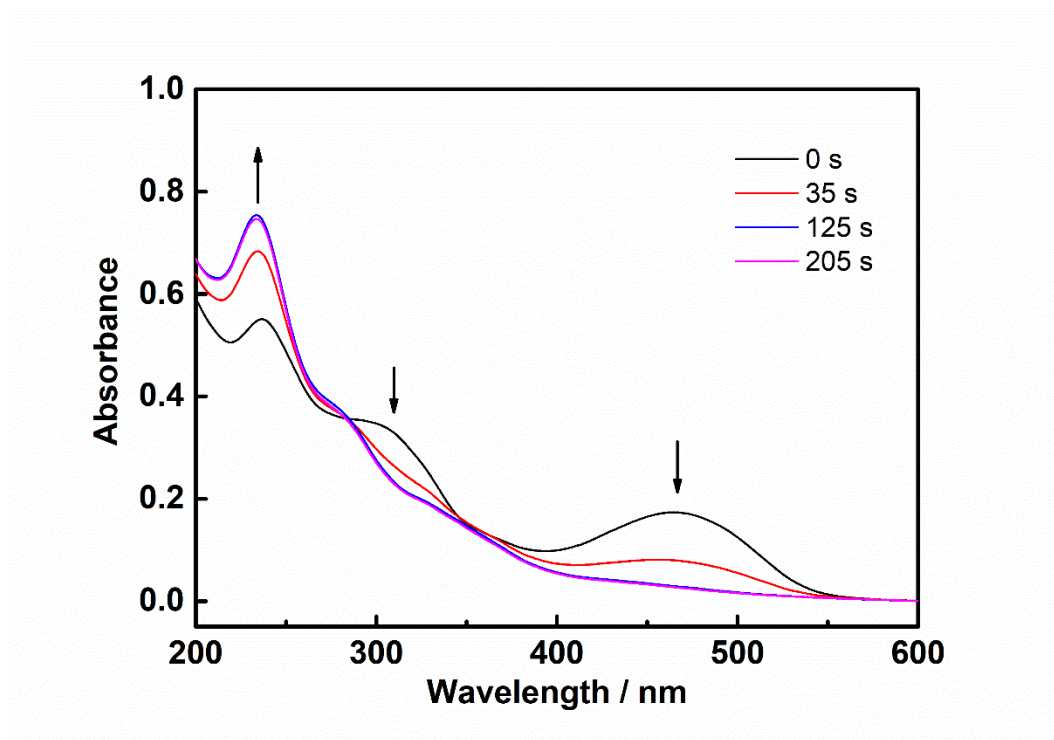


Figure S9. Spectral variations observed upon irradiation (visible light) of **G** at PSS in aqueous solution (5.0×10^{-5} M, 298 K).

Table S1 Crystal data and structure refinement for **CB[10]·Go**

CCDC number	2161361
Empirical formula	$C_{83}H_{96}Cl_2N_{42}O_{20}S_2$
Formula weight	2137.03
Temperature/K	200.00
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	17.3521(10)
$b/\text{\AA}$	18.5203(12)
$c/\text{\AA}$	37.775(3)
$\alpha/^\circ$	90
$\beta/^\circ$	93.165(3)
$\gamma/^\circ$	90
Volume/ \AA^3	12121.1(13)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.171
μ/mm^{-1}	0.930
F(000)	4456.0

Radiation	GaK α ($\lambda = 1.34139$)
2 θ range for data collection/ $^\circ$	4.076 to 102.772
Index ranges	$-20 \leq h \leq 19$, $-20 \leq k \leq 21$, $-43 \leq l \leq 41$
Reflections collected	127466
Independent reflections	19973 [$R_{\text{int}} = 0.1217$, $R_{\text{sigma}} = 0.0812$]
Data/restraints/parameters	19973/385/1349
Goodness-of-fit on F^2	1.084
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0982$, $wR_2 = 0.2228$
Final R indexes [all data]	$R_1 = 0.1340$, $wR_2 = 0.2385$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.95/-1.39

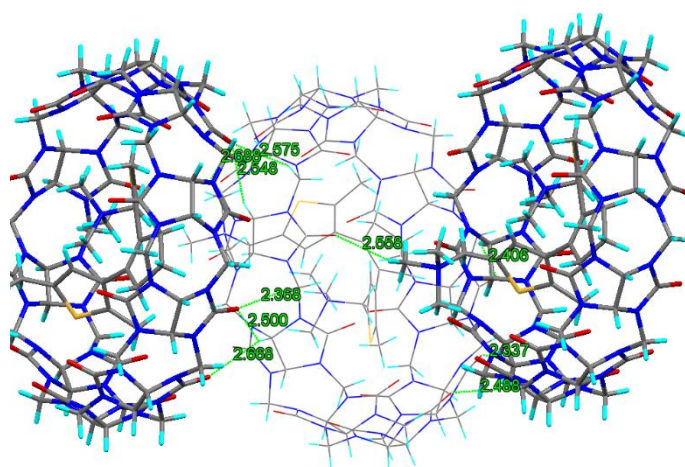


Figure S10. Intermolecular C-H...O interactions among neighboring CB[10] in CB[10]·Go crystal.

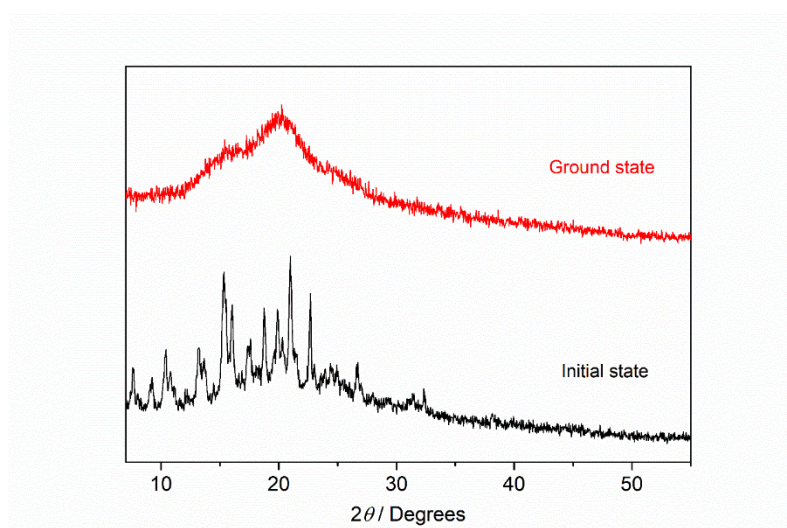


Figure S11. Powder X-ray diffraction (PXRD) pattern of CB[10]·Go powder before and after grinding.

References

1. X. Yang, Z. Zhao, X. Zhang, S. Liu, *Sci. China Chem.* 61 (2017) 787-791.
2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* 42 (2009) 339-341.
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