Host-guest interaction-induced selective oxidation inside aqueous Pd_6L_4 cage

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Contents:

1.1 Materials and Methods:

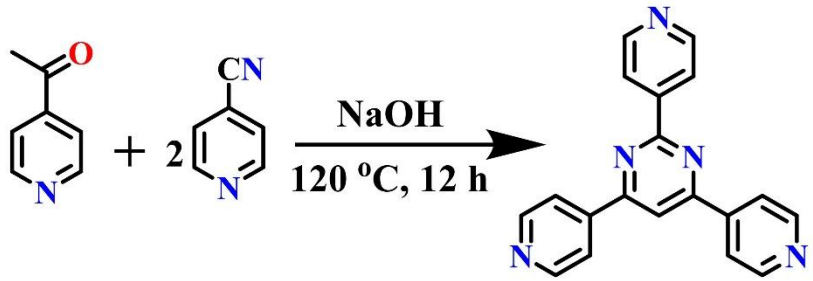
General chemicals and solvents were purchased from commercially available suppliers and were used without further purification. All the reactions, unless otherwise mentioned, were carried out under ambient conditions in normal atmosphere. The NMR spectra of the newly prepared materials were recorded on BRUKER 400 MHz and/or 500 MHz spectrometers. The chemical shifts (δ) in the ^{1}H NMR spectra were reported in ppm relative to the tetramethylsilane, which was used as an internal standard (δ = 0.00 ppm) or the resonance of the proton resulting from partial deuteriation of the NMR solvents: D_2O (δ = 4.79 ppm), $CDCl_3$ (δ = 7.26 ppm), CD_3CN (δ = 1.94 ppm) and DMSO-d_6 (δ = 2.50 ppm). ^{13}C NMR spectra were recorded using the same instruments at 100 MHz, 125 MHz and all the chemical shifts (δ) were reported in ppm relative to external $CDCl_3$ at 77.8-77.2 ppm. Electrospray ionization mass spectra were recorded using Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer along with the use of standard spectroscopic grade solvents.

1.2 Synthetic Strategy:

1.2.1 Synthesis of Ligand L

4-Acetylpyridine (1g, 8.25 mmol) and NaOH (0.4 g, 10.03 mmol) were taken in a mortar and mixed uniformly using a pestle until a brown viscous oil was formed. Then 4-

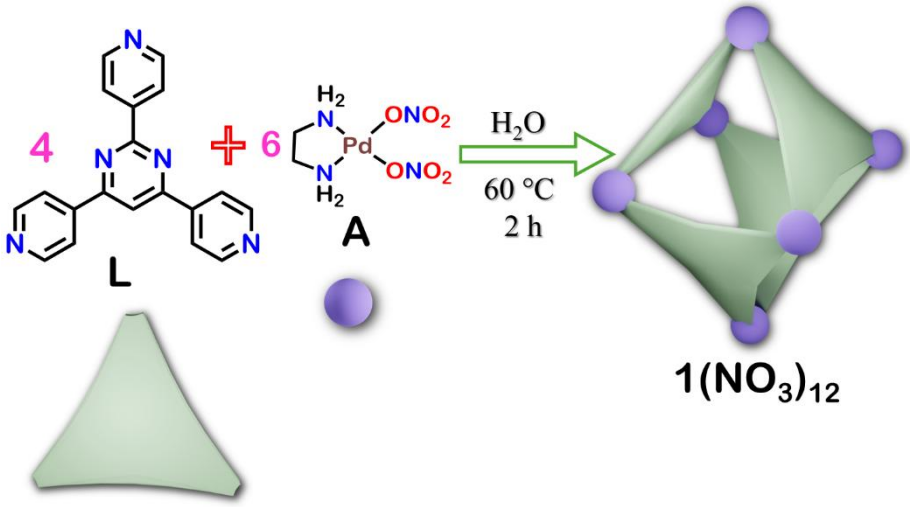
Pyridinecarbonitrile (1.72g, 16.51 mmol) was added to it and the mixture was mixed thoroughly with the pestle until a yellowish-brown solid was formed. The mixture was then transferred to a Teflon-lined stainless-steel reactor and capped. It was then heated at 120°C for 12 hours in a furnace. Upon completion of reaction, a brown solid was obtained which was then extracted with water and filtered. The filtered precipitate was washed thoroughly with water and 20% NaOH solution. The resulting white residue contained the ligand **L** and was further purified by column chromatography (Silica gel 60-120 mesh, $CHCl_3$/THF solvent). Isolated yield: 1 g (39%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.90 (d, 4H), 8.88 (d, 2H), 8.54 (d, 2H), 8.21 (s, 1H), 8.16 (d, 4H).^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 163.79, 151.03, 150.59, 143.65, 122.25, 121.12, 112.48. HRMS (ESI): $C_{19}H_{13}N_5$, $[M+Na+CH_3OH]^+$ = 366.1331 (calculated) Found: 366.1016.



Scheme S1: Schematic representation of the synthesis of the ligand **L**.

1.2.2 Synthesis of Cage 1

In a 4 mL glass vial, cis-[(en)Pd(NO_3)$_2$] **A** (35 mg, 0.012 mmol) and **L** (25 mg, 0.08 mmol) were added in 2 mL Millipore water. The mixture was heated at 60 °C until a clear colourless solution was obtained. Yield: 54 mg (90%). ^{1}H NMR (D_2O, 500 MHz): δ (ppm) 9.01(b, 6H), 8.54-8.57 (b, 3H), 8.35(b, 4H), 2.98(s, 6H). ESI-MS (CH_3CN) m/z = 1121.4307 for $[A_6L_4(NTf_2)_8]^{4+}$ (calc. 1121.4201), 1588.5493 for $[A_6L_4(NTf_2)_9]^{3+}$ (calc. 1588.5306).



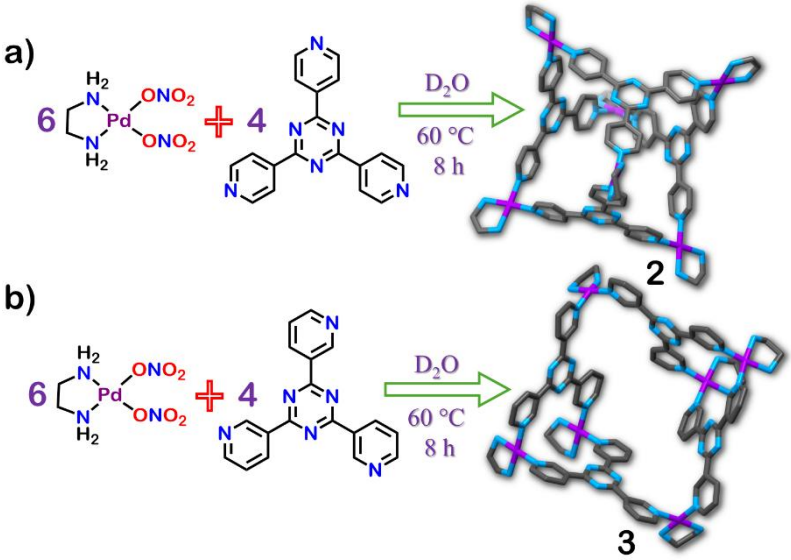
Scheme S2: Schematic representation for the synthesis of **1**.

1.2.3 Synthesis of Cage 2

In a 4 mL glass vial, ligand 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (5 mg, 16.01 µmol) was added to 0.5 mL D_2O solution of $[Pd^{II}(en)](NO_3)_2$ (6.98 mg, 24.01 µmol) [en = Ethylenediamine]. The mixture was heated at 60 °C for 8 hours, which resulted in a clear solution. This clear solution was then used as it is for characterization and reaction. ^{1}H NMR and ESI-MS matched with previously reported literature results.[S2]

1.2.4 Synthesis of Cage 3

In a 4 mL glass vial, a similar reaction procedure as applied for the synthesis of **2** was followed. Only isomeric ligand 2,4,6-tri(pyridin-3-yl)-1,3,5-triazine (5 mg, 16.01 µmol) was used instead. ^{1}H NMR and ESI-MS matched with previously reported literature results.[S3]



Scheme S3: Schematic representation for the synthesis of a) cage **2** and b) cage **3**.

2. Spectral Characterization of Ligand (L):

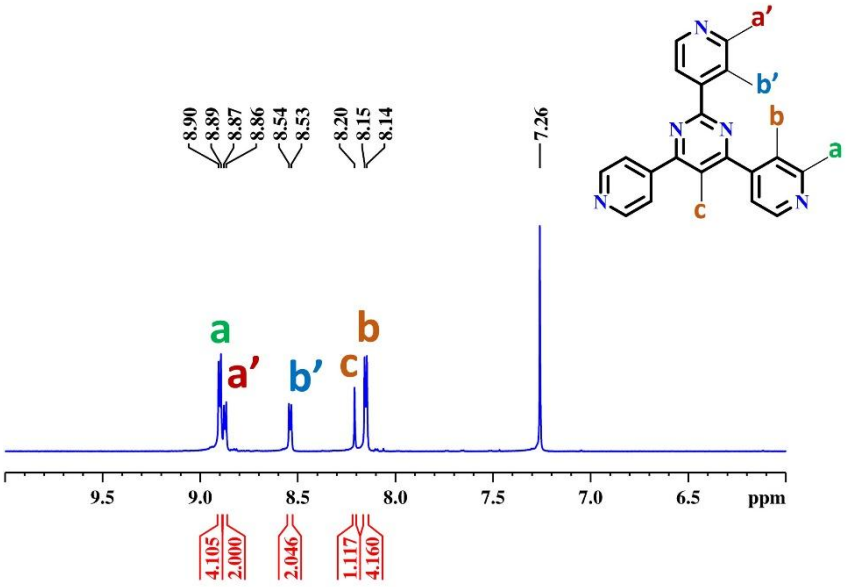


Fig. S1: ^{1}H-NMR spectrum of ligand **L** in $CDCl_3$.

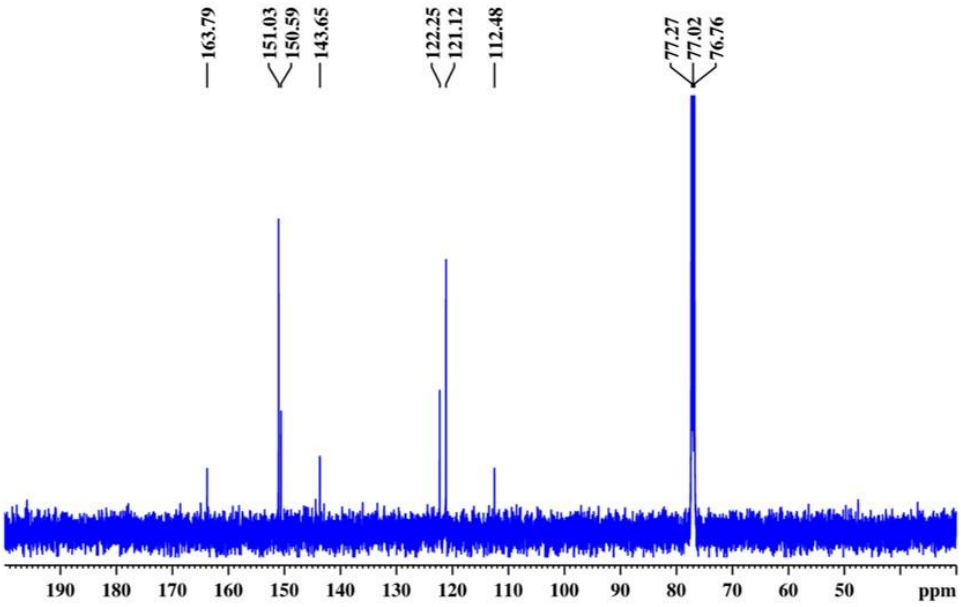


Fig. S2: ^{13}C NMR spectrum of **L** in $CDCl_3$.

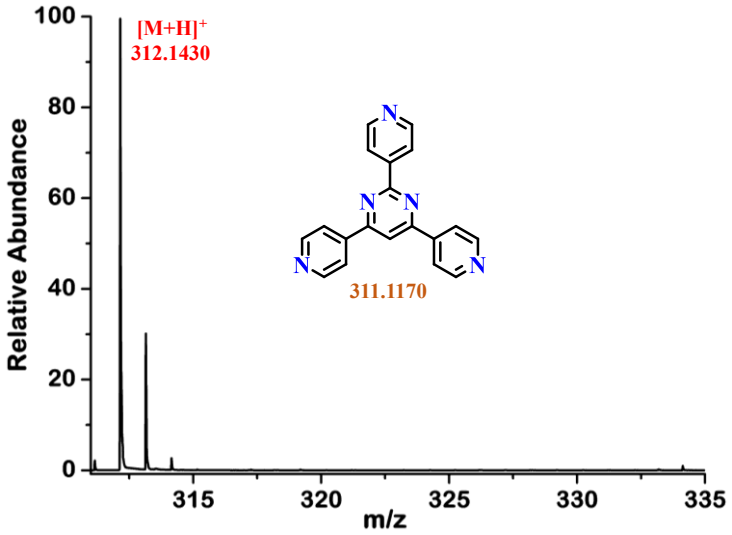


Fig. S3: ESI-MS spectrum of **L** in MeOH.

3. Spectral Characterization of 1:

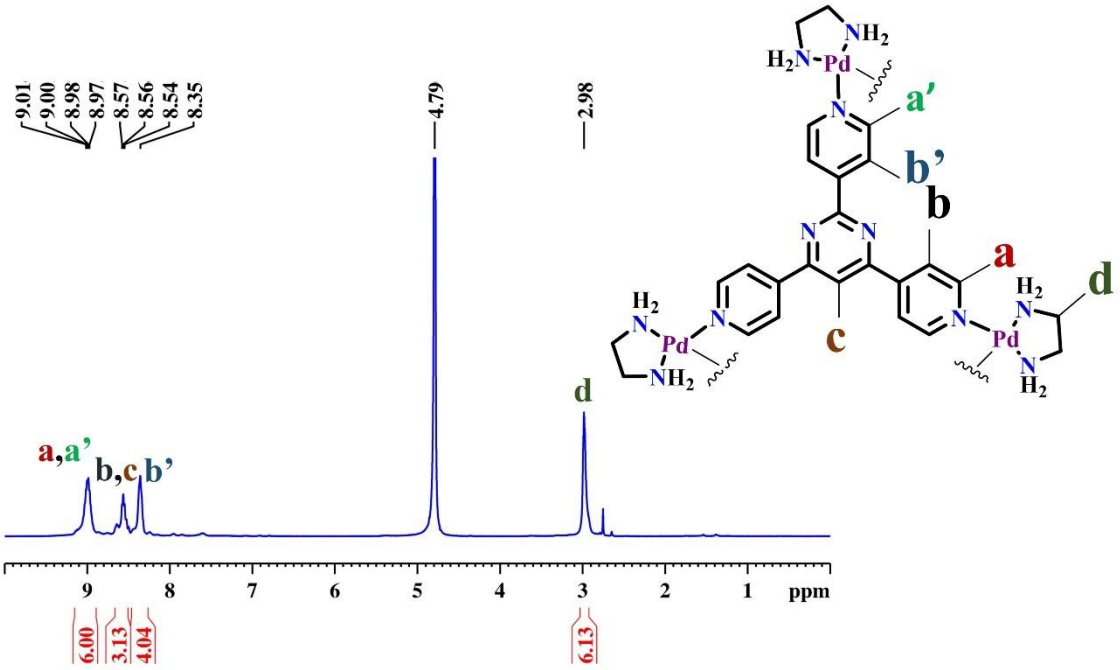


Fig. S4: ^{1}H NMR spectrum of **1** in D_2O.

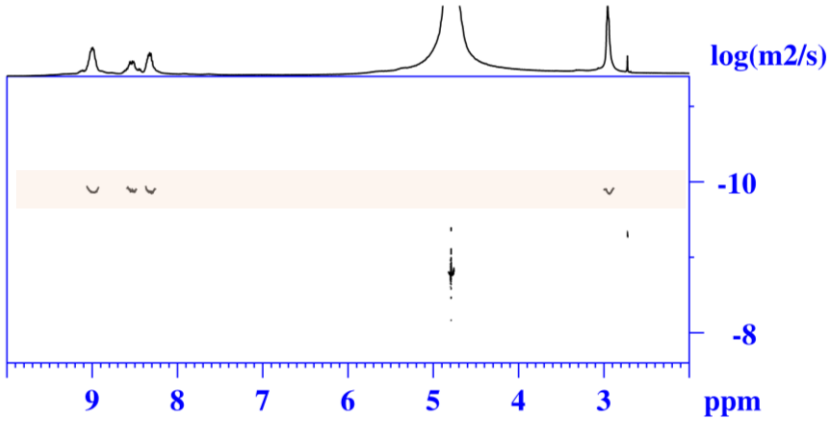


Fig. S5: ^{1}H DOSY NMR spectrum of **1** in D_2O.

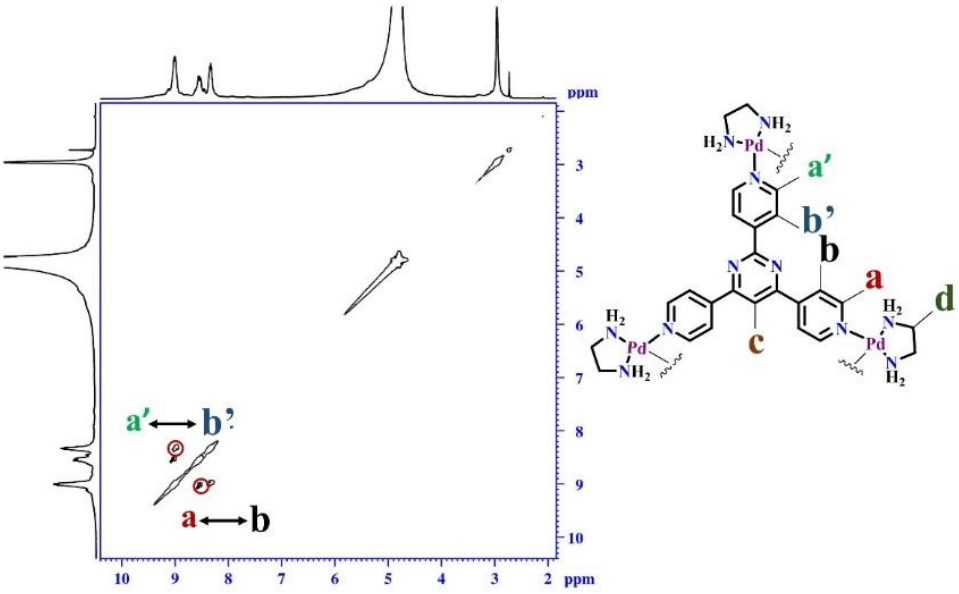


Fig. S6: ^{1}H-^{1}H COSY NMR spectrum of **1** in D_2O.

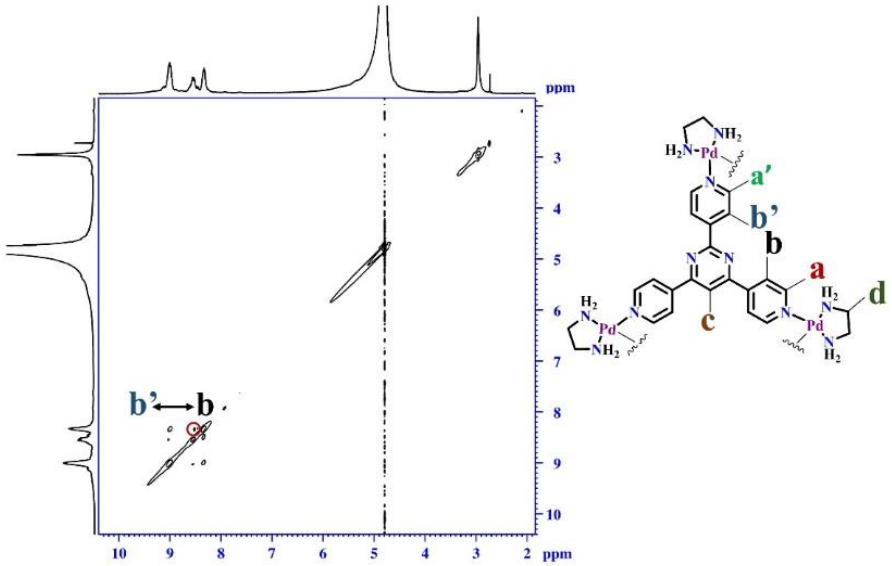


Fig. S7: ^{1}H-^{1}H NOESY NMR spectrum of **1** in D_2O.

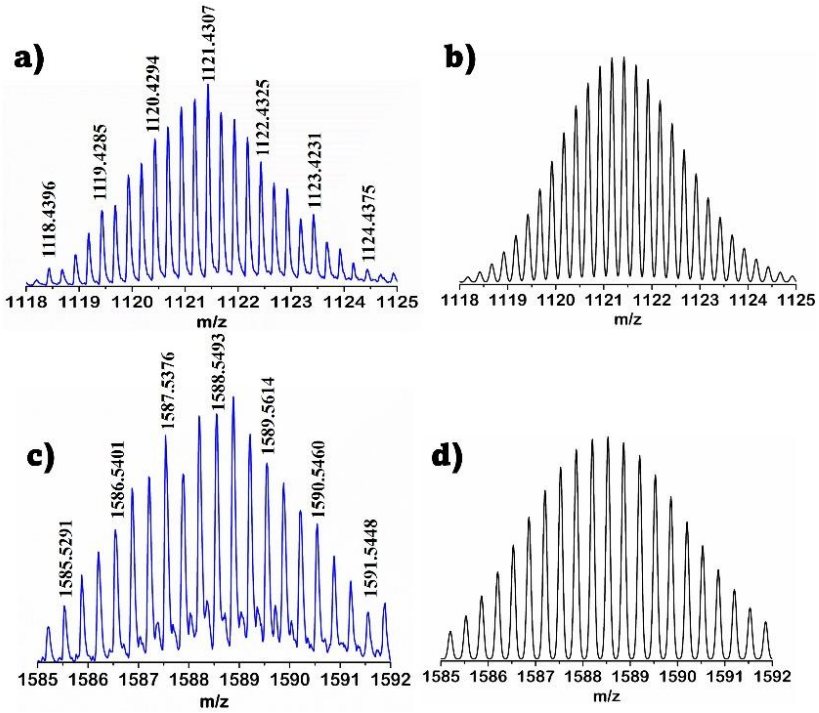


Fig. S8: Isotopic distribution patterns of the peaks corresponding to (a) $[\mathbf{A_6L_4}(PF_6)_8]^{4+}$ and (b) $[\mathbf{A_6L_4}(PF_6)_9]^{3+}$ fragments (blue experimental and black calculated).

4. Host-Guest Chemistry of 1:

4.1 General Procedure for Host-Guest Complex:

The host-guest complexes of **1** were obtained in two different ways:

(a) **In-situ complexation**: In a clean 4 mL glass vial a mixture of **A** (7 mg, 24.09 µmol), **L** (5 mg, 16.06 µmol), and the desired guest (5 mg, excess) was taken followed by the addition of 0.5 mL D_2O. The mixture was then stirred for 12 hours at 65 °C and got the yellow turbid solution. The excess guest was removed via centrifugation. The clear yellow supernatant was then isolated and characterized by ^{1}H NMR spectroscopy.

(b) **Complexation after the formation of the cage**: In a clean 4 mL glass vial a mixture of the acceptor **A** (7 mg, 24.09 µmol), and the ligand **L** (5 mg, 16.06 µmol) was taken followed by the addition of 0.5 mL D_2O. The mixture was then stirred for 12 hours at 65 °C and got the colorless clear solution of the **1**. The solution was then mixed with the desired guest (5 mg, excess) and stirred overnight at 50 °C. The resultant solution was then isolated by centrifugation and characterized by ^{1}H NMR spectroscopy.

The ^{1}H NMR obtained from both methods gave the same product and hence any one of the methods could be used to obtain host-guest complex.

Xanthene (**X**) was encapsulated in the aqueous cage **1** and characterized by ^{1}H NMR and further verified by the single diffusion band in the ^{1}H DOSY experiment of **X⊂1.**

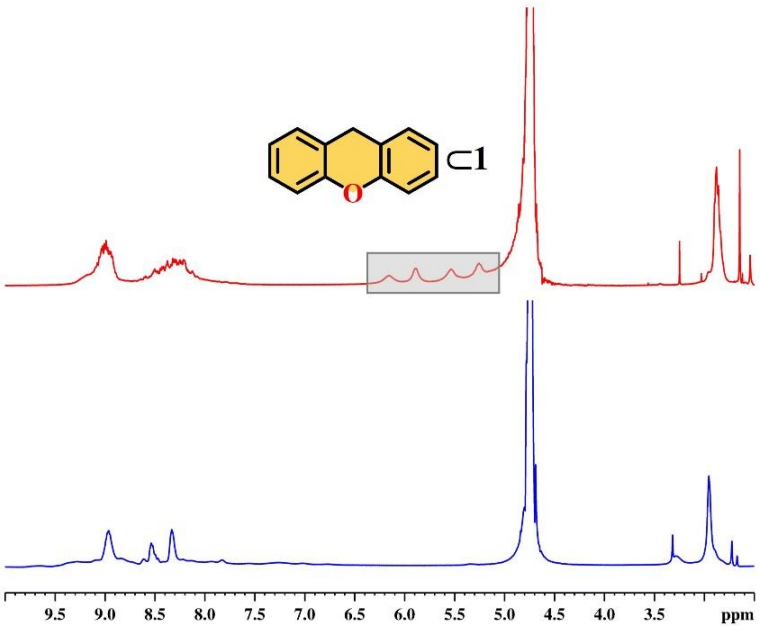


Fig. S9: ^{1}H NMR spectra of **1** and the host-guest complex **X⊂1** (**X**: Xanthene)) in D_2O.

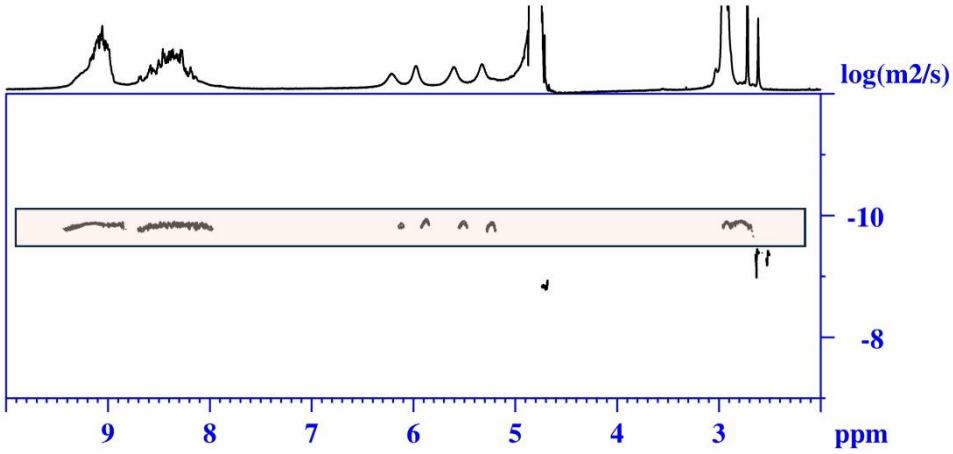


Fig. S10: ^{1}H DOSY NMR spectrum of **X⊂1** (**X**: Xanthene)) in D_2O.

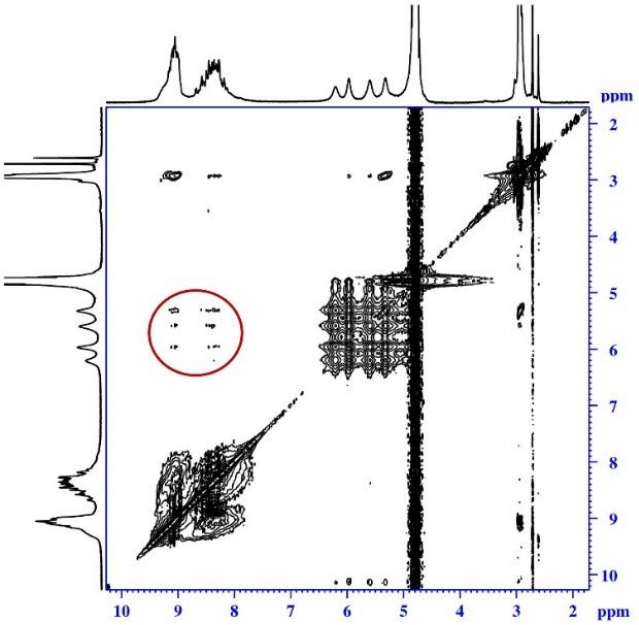


Fig. S11: ^{1}H-^{1}H NOESY NMR spectrum of **X⊂1** in D_2O. The red mark indicates the interaction between the host and guest peak

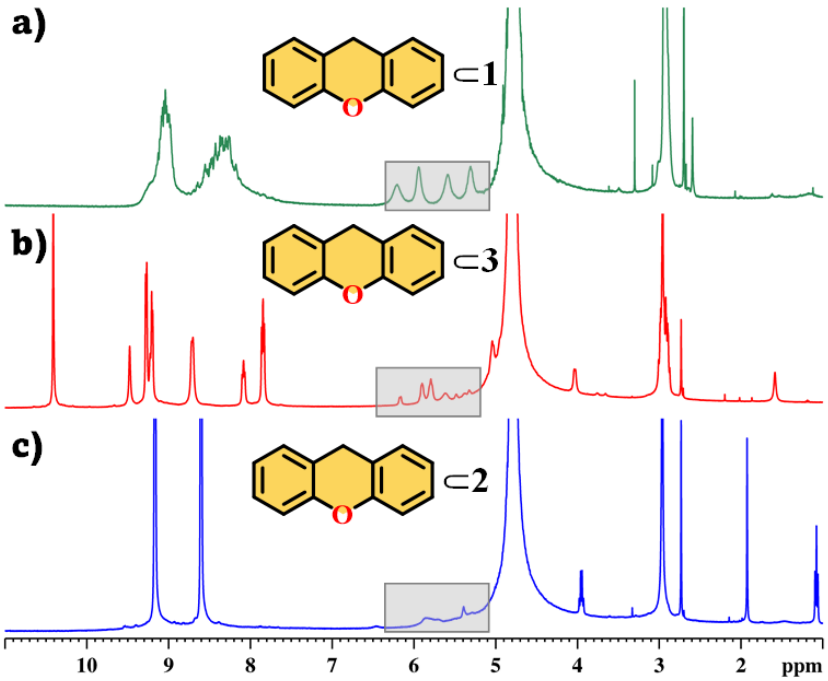


Fig. S12: ^{1}H NMR spectra of the host-guest complexes a) **X⊂1**, b) **X⊂3**, and c) **X⊂2** (**X**: Xanthene) in D_2O.

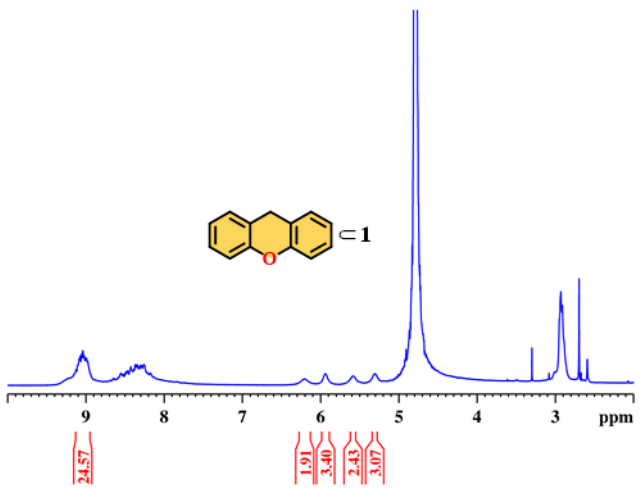


Fig. S13: ^{1}H NMR spectrum of **X⊂1** in D_2O showing the integration of host and guest to determine the stoichiometry of the host-guest complex (1:1).

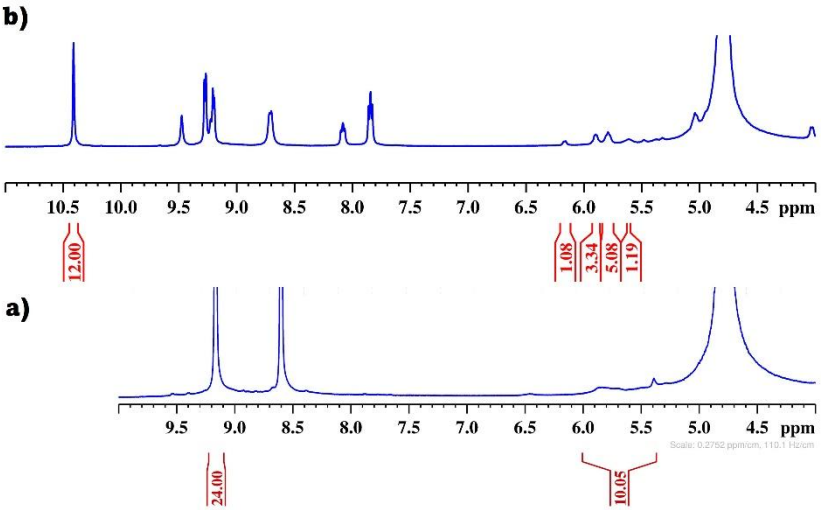
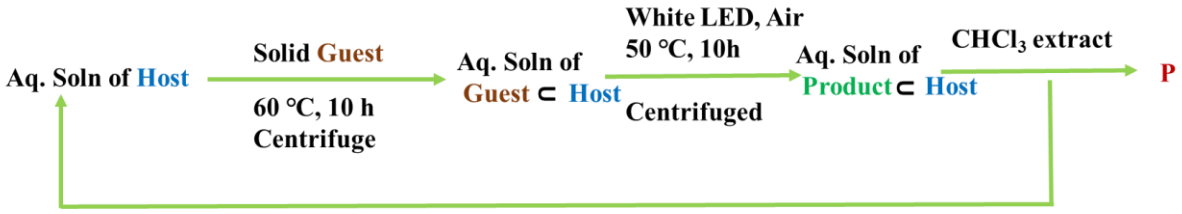


Fig. S14: ^{1}H NMR spectra of a) **X⊂2**, b) **X⊂3** in D_2O showing the integration of host and guest to determine the stoichiometry of the host-guest complex (1:1).

5. Oxidation of the guest molecules inside the cage 1:

The oxidation of the guest molecules inside **1** was probed by taking a 0.5 mL of aqueous solution of the cage in a 4 mL glass vial. And then solid guest was added (excess 5mg) and stirred the rection at 50 °C for 10 h. The host-guest complex was centrifuged to remove the excess guest molecule, and a clear supernatant was used for the oxidation. The reaction was then stirred in the presence of white light (45 W LED (λ > 400 nm)) for 10 hours at 50 °C. After the completion of the reaction, 0.5 mL of $CDCl_3$ was added to it and the reaction was stirred for 15-20 minutes and the ^1H NMR of the guest was recorded. As the guest is removed from the host, it could be used again for another reaction.



Scheme S4: Schematic representation of the reaction procedure using cage **1**.

6. Spectral characterization of the oxidized alkyl arenes inside 1

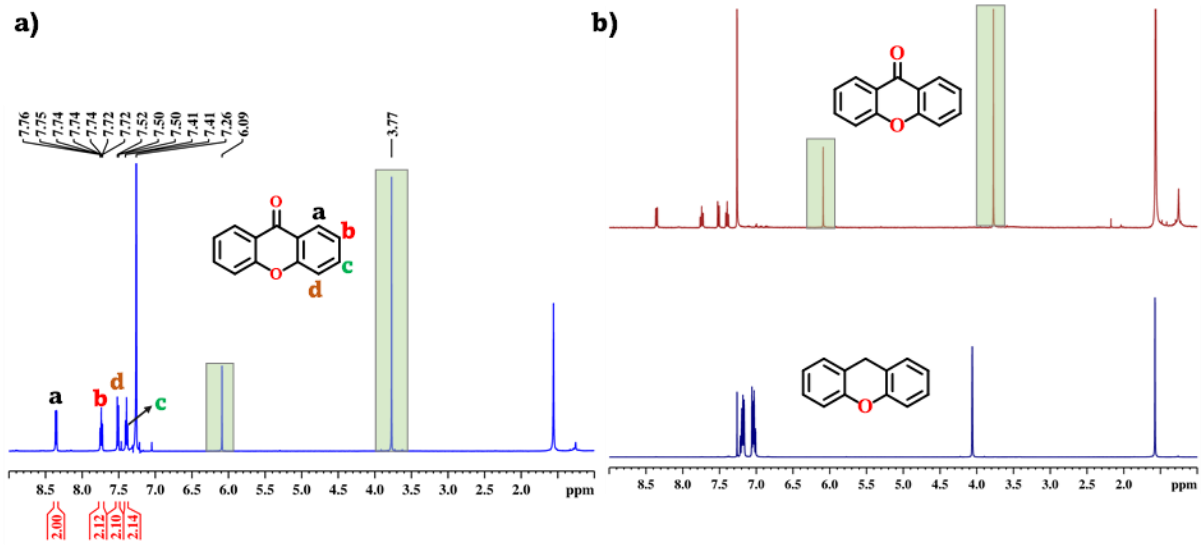


Fig. S15: (a) ^1H NMR spectrum of xanthone (**XO**), and (b) the stacked ^1H NMR spectra of xanthone and xanthene in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

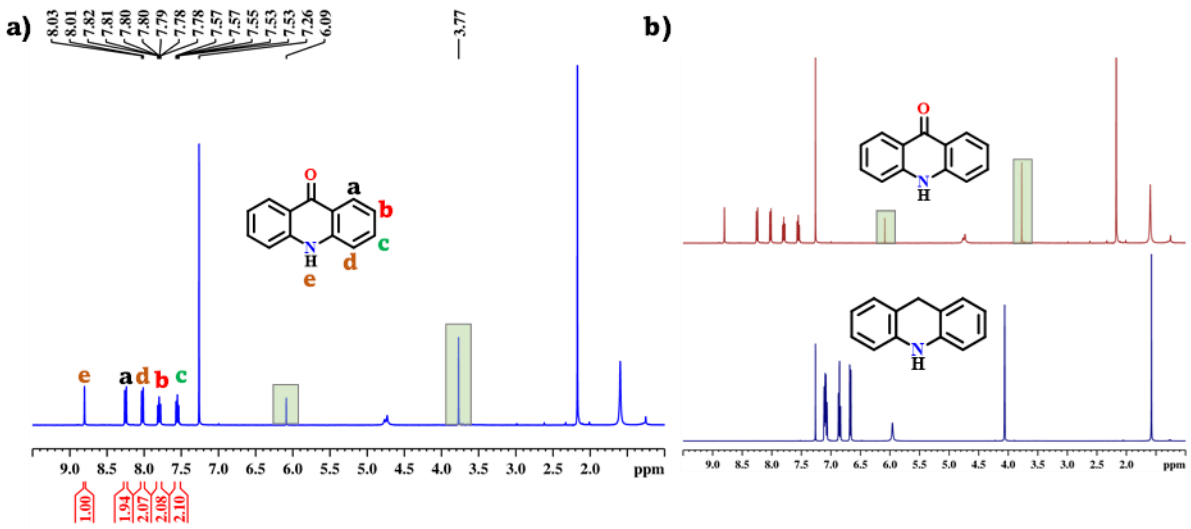


Fig. S16: (a) ^{1}H NMR spectrum of acridone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of acridone and acridine in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

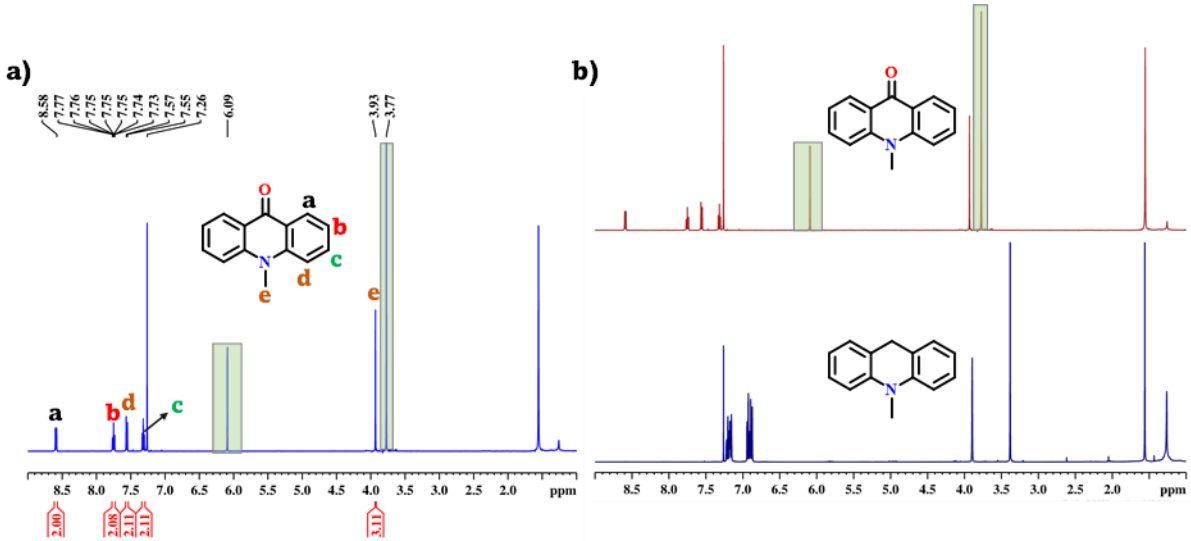


Fig. S17: (a) ^{1}H NMR spectrum of methyl acridone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of methyl acridone and methyl acridine in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

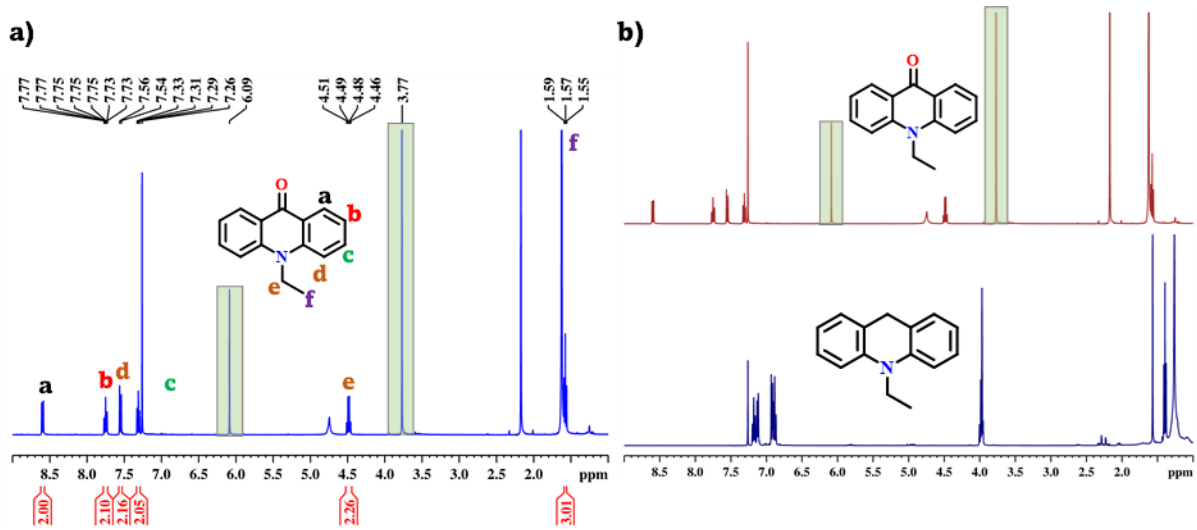


Fig. S18: (a) ^{1}H NMR spectrum of ethyl acridone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of ethyl acridone and ethyl acridine in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

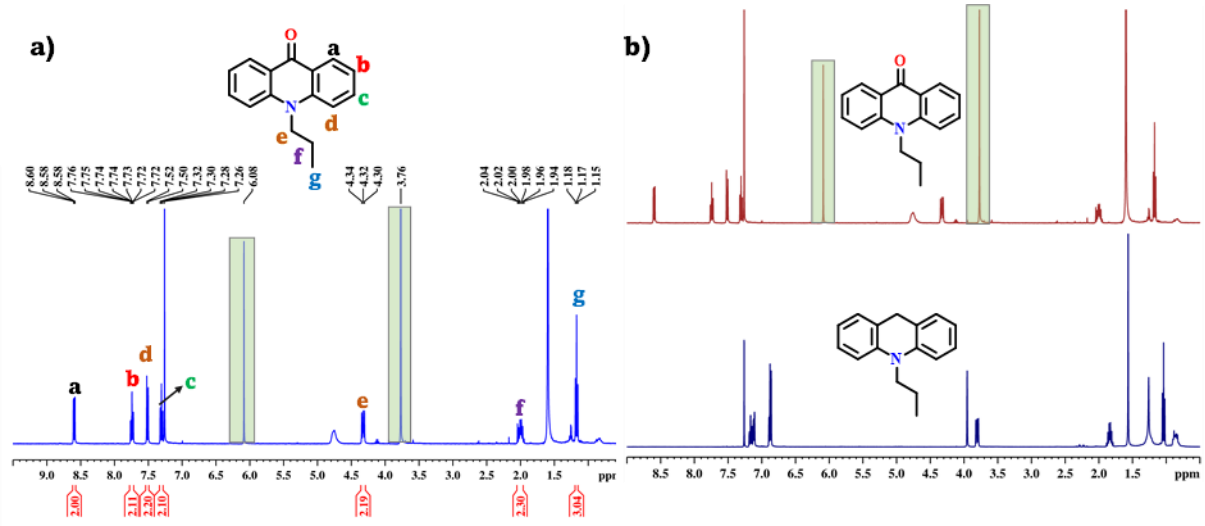


Fig. S19: (a) ^{1}H NMR spectrum of propyl acridone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of propyl acridone and propyl acridine in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

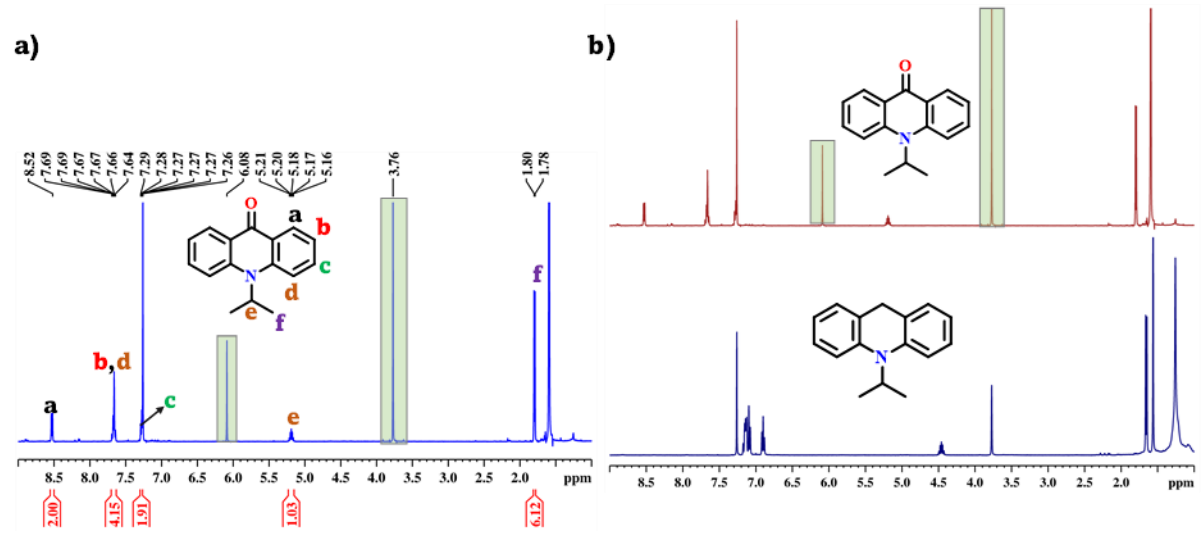


Fig. S20: (a) ^{1}H NMR spectrum of isopropyl acridone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of isopropyl acridone and isopropyl acridine in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

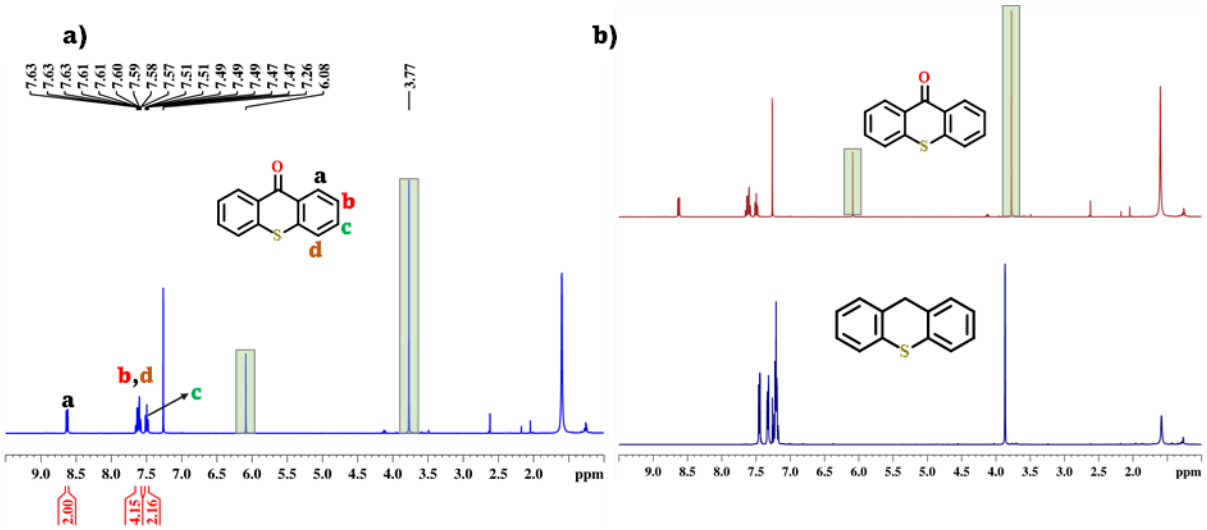


Fig. S21: (a) ^{1}H NMR spectrum of thioxanthone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of thioxanthone and thioxanthene in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

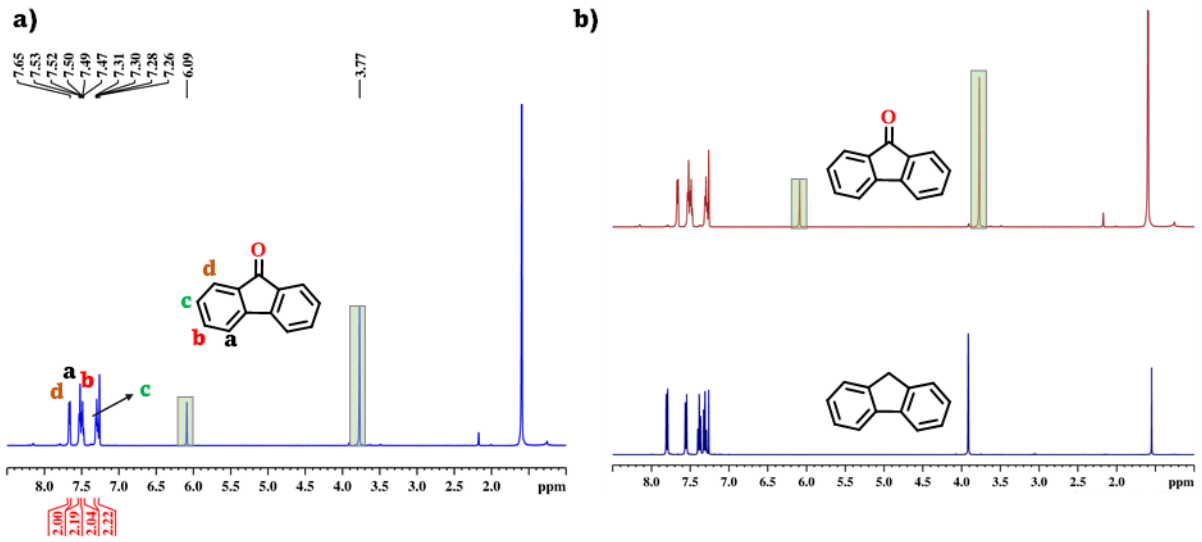


Fig. S22: (a) ^{1}H NMR spectrum of 9-fluorenone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of 9-fluorenone and fluorene in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

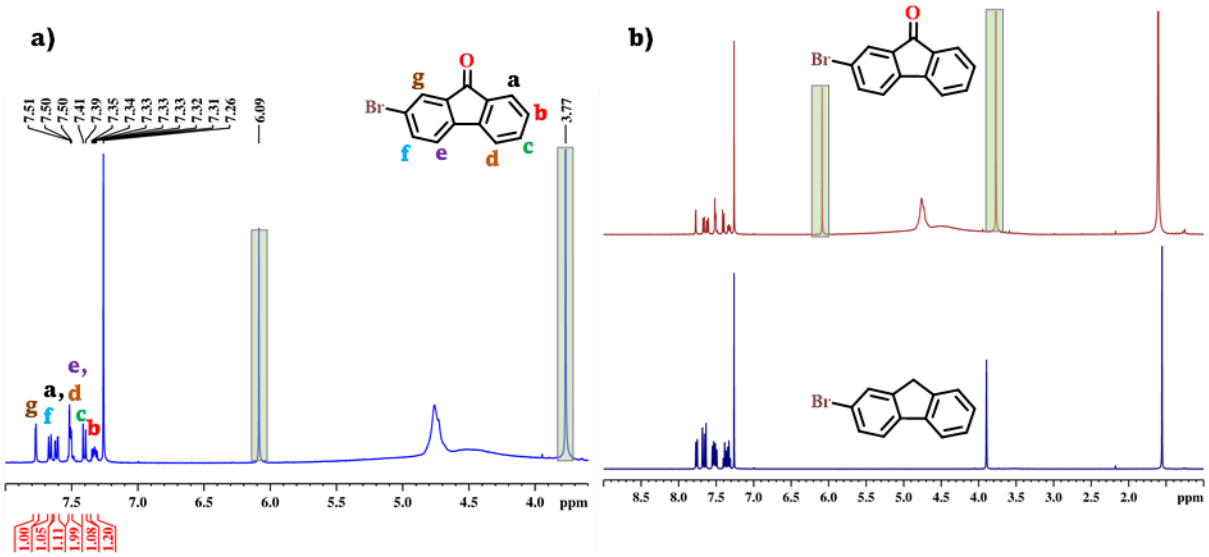


Fig. S23: (a) ^{1}H NMR spectrum of 2-bromo-9-fluorenone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of 2-bromo-9-fluorenone and 2-bromo-9-fluorene in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

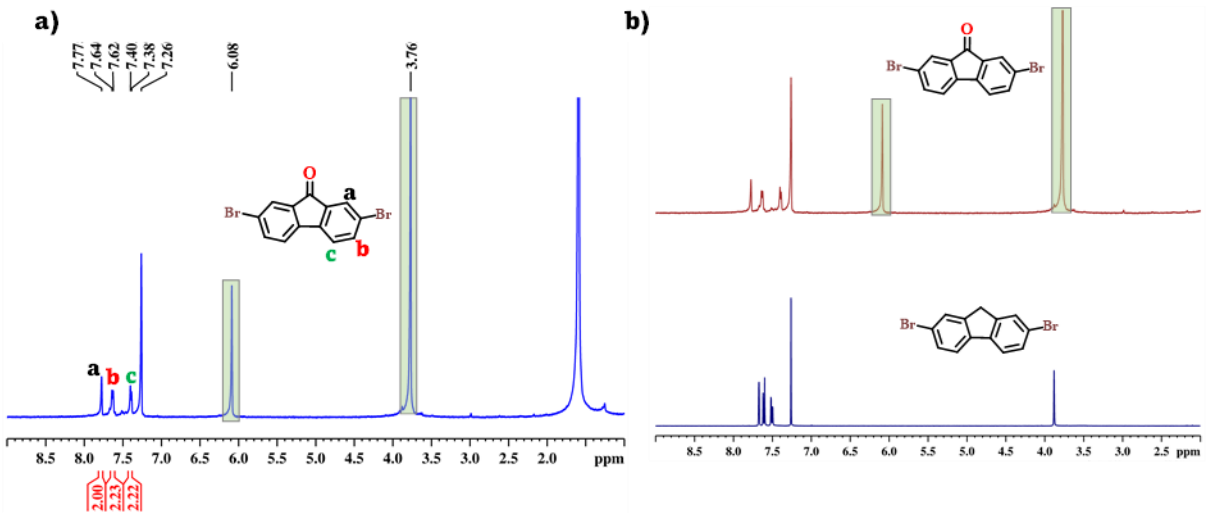


Fig. S24: (a) ^{1}H NMR spectrum of 2,7-dibromo-9-fluorenone in $CDCl_3$, and (b) the stacked ^{1}H NMR spectra of 2,7-dibromo-9-fluorenone and 2,7-dibromo-9-fluorene in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

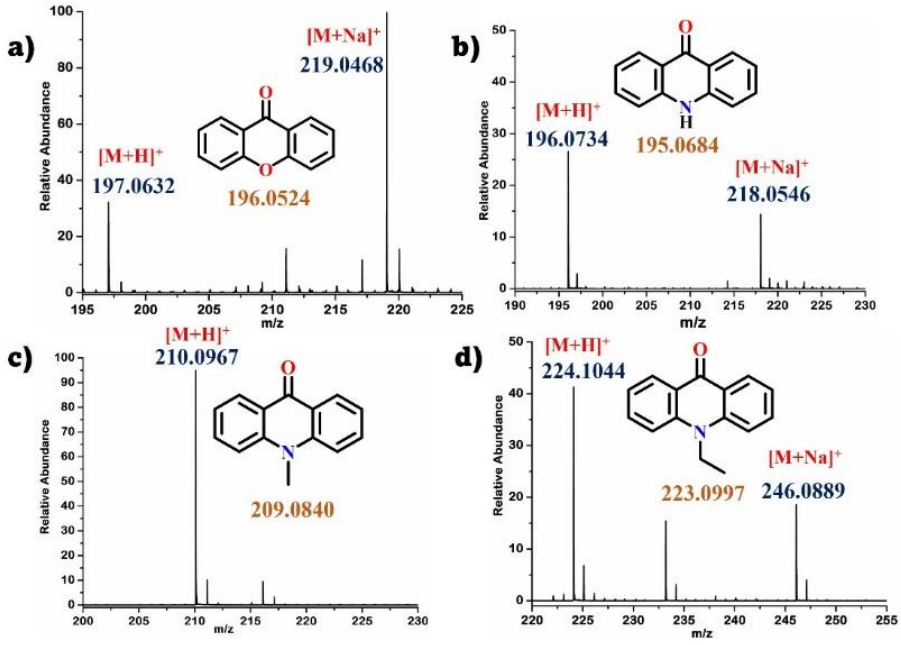


Fig. S25: ESI-MS spectra of oxidized products (a) xanthone, (b) acridone, (c) methyl acridone, (d) and ethyl acridone.

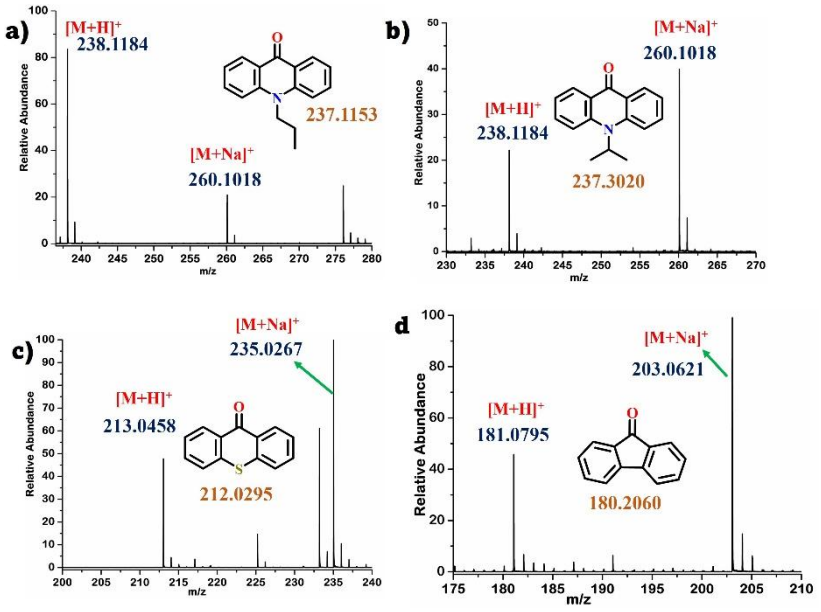


Fig. S26: ESI-MS spectra of oxidized products (a) propyl acridone, (b) isopropyl acridone, (c), thioxanthone, and (d) fluorenone.

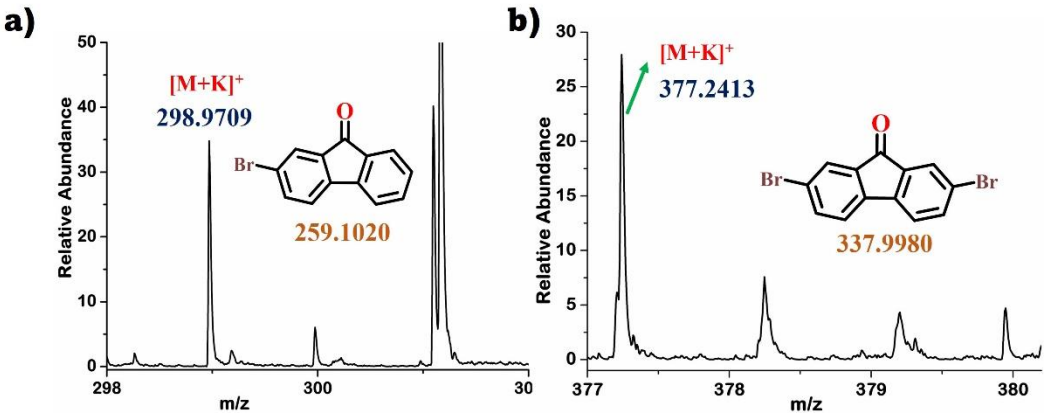


Fig. S27: ESI-MS spectra of the oxidized products (a) 2-bromofluorenone, and (b) 2,7-dibromofluorenone.

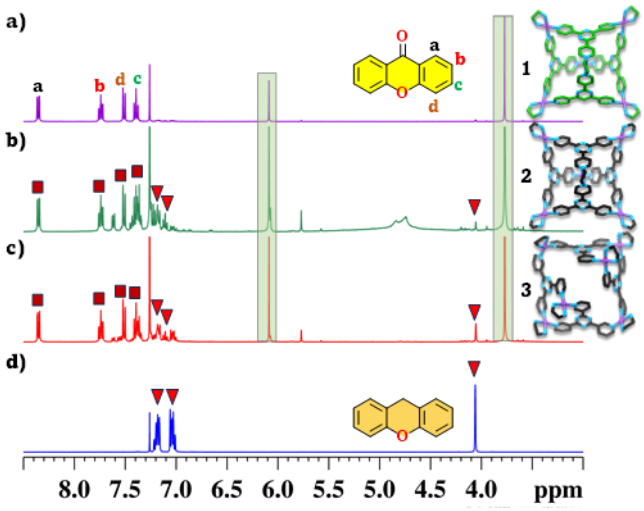


Fig. S28: Partial ^{1}H NMR plot of a) the product obtained from **1** (recorded in $CDCl_3$), b) the product obtained from **2 (**recorded in $CDCl_3$), and c) the product obtained from **3** (recorded in $CDCl_3$). Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green, and the squares denote the product peaks and triangles denote the starting material peaks.

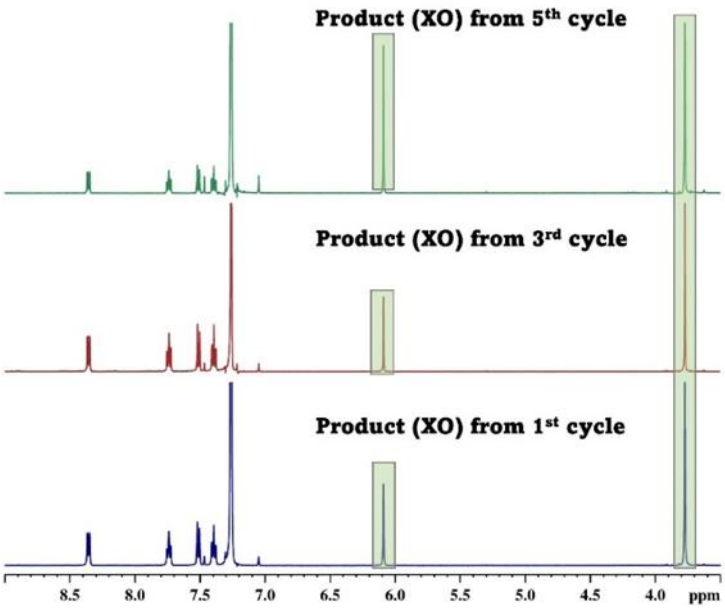


Fig. S29: Partial ^{1}H NMR stack plot of the oxidized product xanthone (**XO)** in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

6. Monitoring the formation of the oxidized product with time:

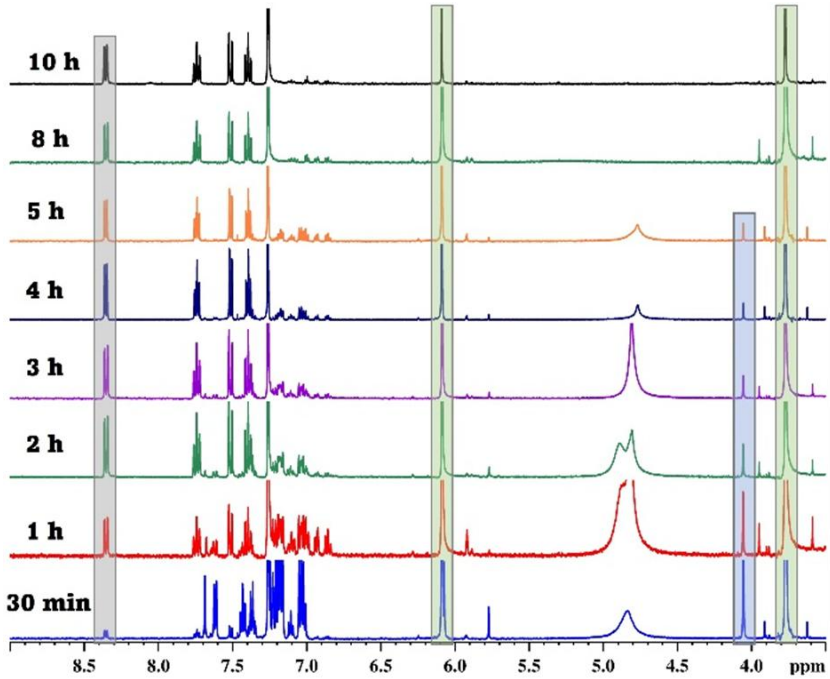


Fig. S30. Partial ^{1}H NMR stack plot of the oxidized product xanthone (**XO)** in $CDCl_3$, the reaction was monitored by NMR with time 30 minutes to 10 hours. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green; the gray highlighted peak corresponds to the product and the blue highlighted peak corresponds to the reactant.

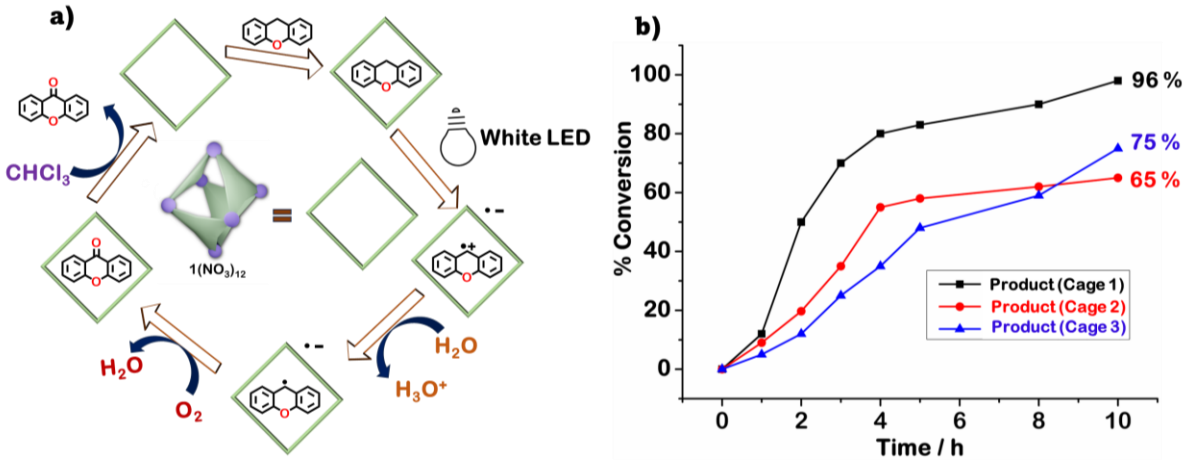
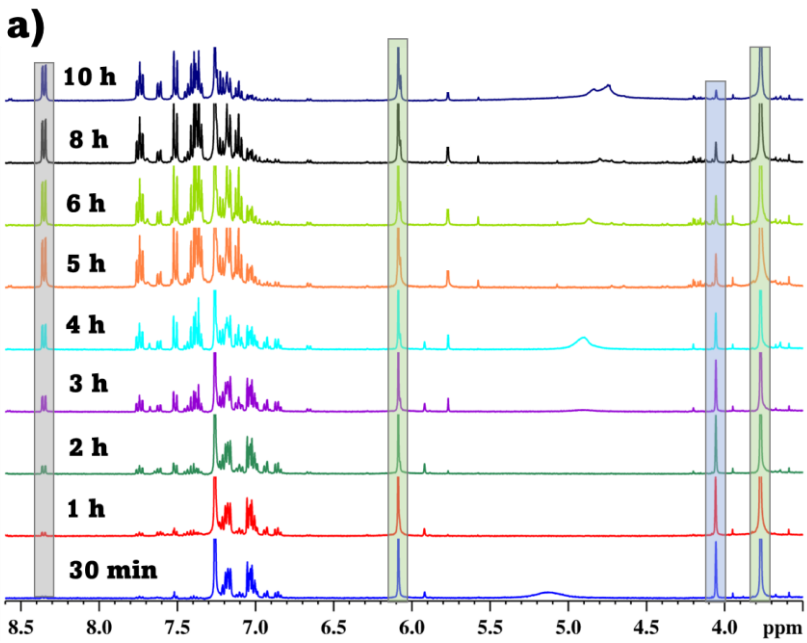


Fig. S31. (a) White-light triggered oxidation of benzylic C(sp^3)-H inside cage **1** and the corresponding chemical transformation path of the plausible mechanism and (b) time-course plot of the xanthene oxidation inside **1**, **2**, and **3**.



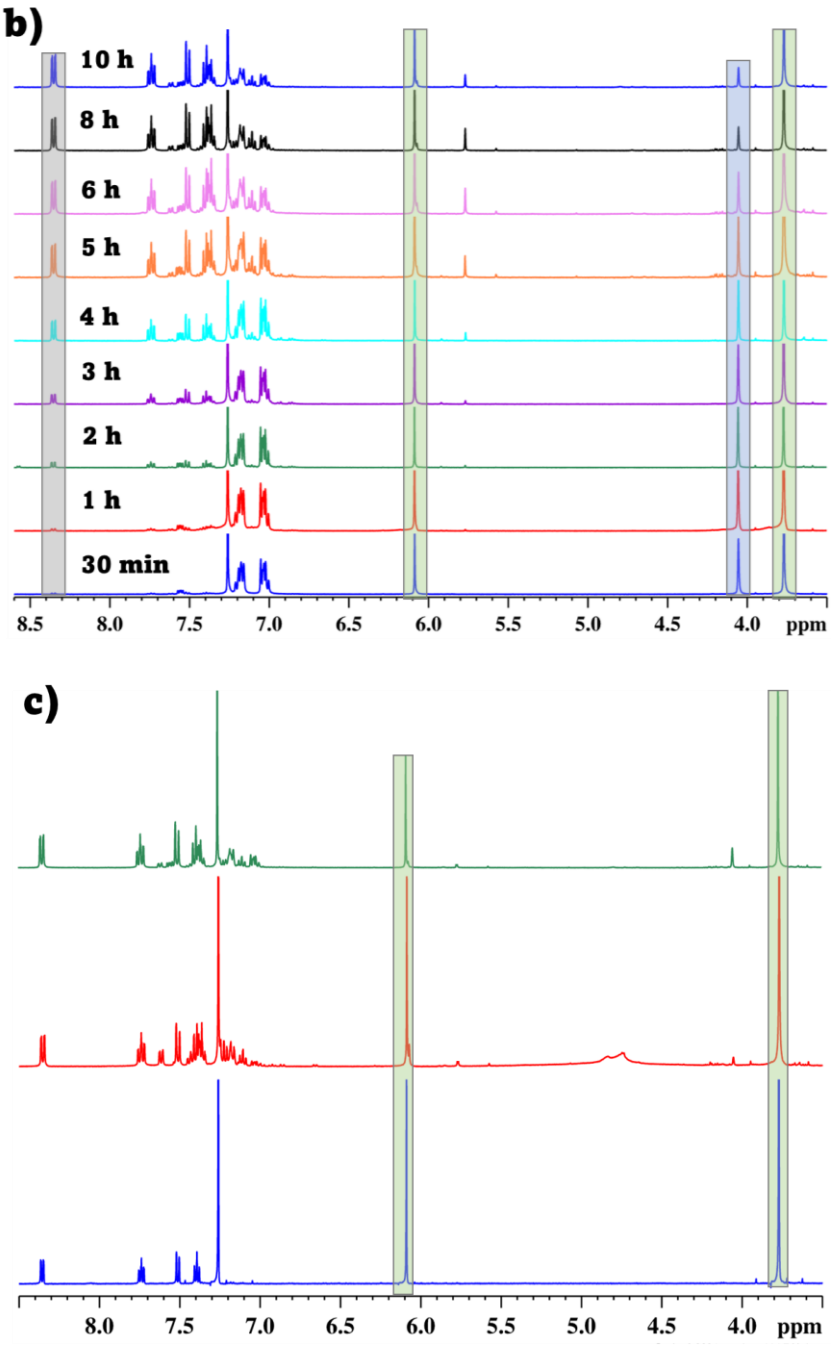


Fig. S32. (a) Partial ^{1}H NMR stack plot of the oxidized product xanthone (**XO)** in $CDCl_3$ by **2**, b) the product obtained by **3** in $CDCl_3$, and c) partial ^{1}H NMR stack plot of the oxidized product after 10 h by cages **1** (blue), **2** (red), and **3** (green) in $CDCl_3$.The reaction was monitored by ^{1}H NMR with time 30 minutes to 10 hours. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green; the gray highlighted peak corresponds to the product and the blue highlighted peak corresponds to the reactant.

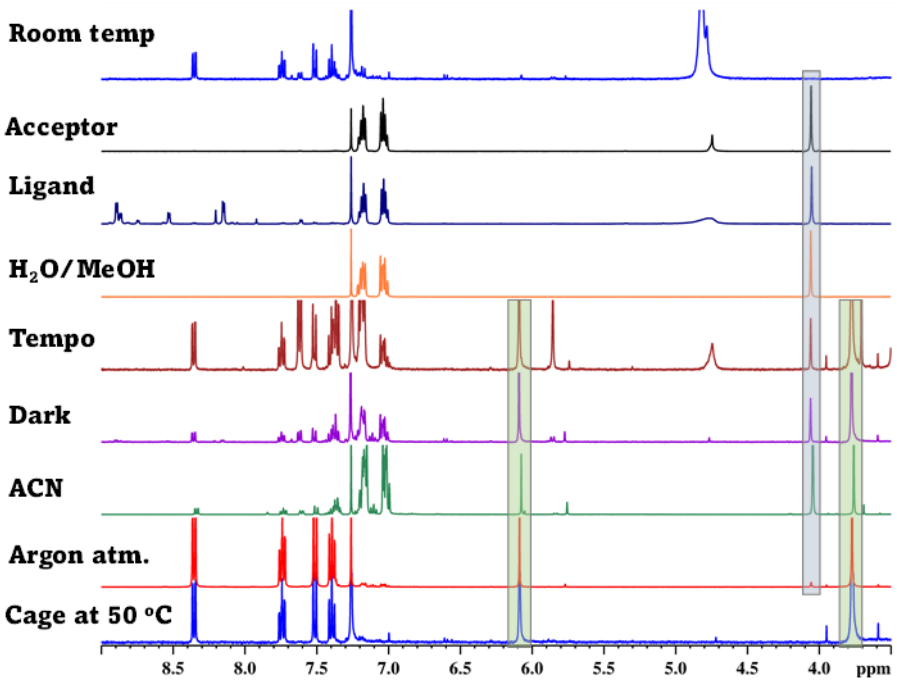


Fig. S33: Partial ^{1}H stack plot of products obtained from **1**, using different conditions as listed in **Table 1** (Main Text) in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green, and the peak is highlighted in gray for the starting material (**X**).

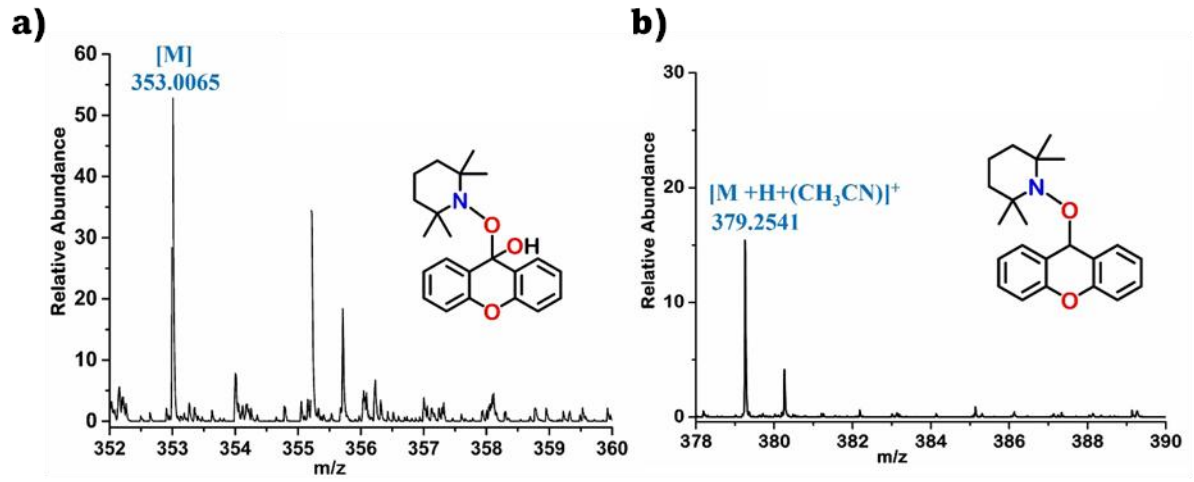


Fig. S34: ESI-MS spectra of the TEMPO adduct with xanthene after photoreaction inside cage **1** with 400 nm LED light source.

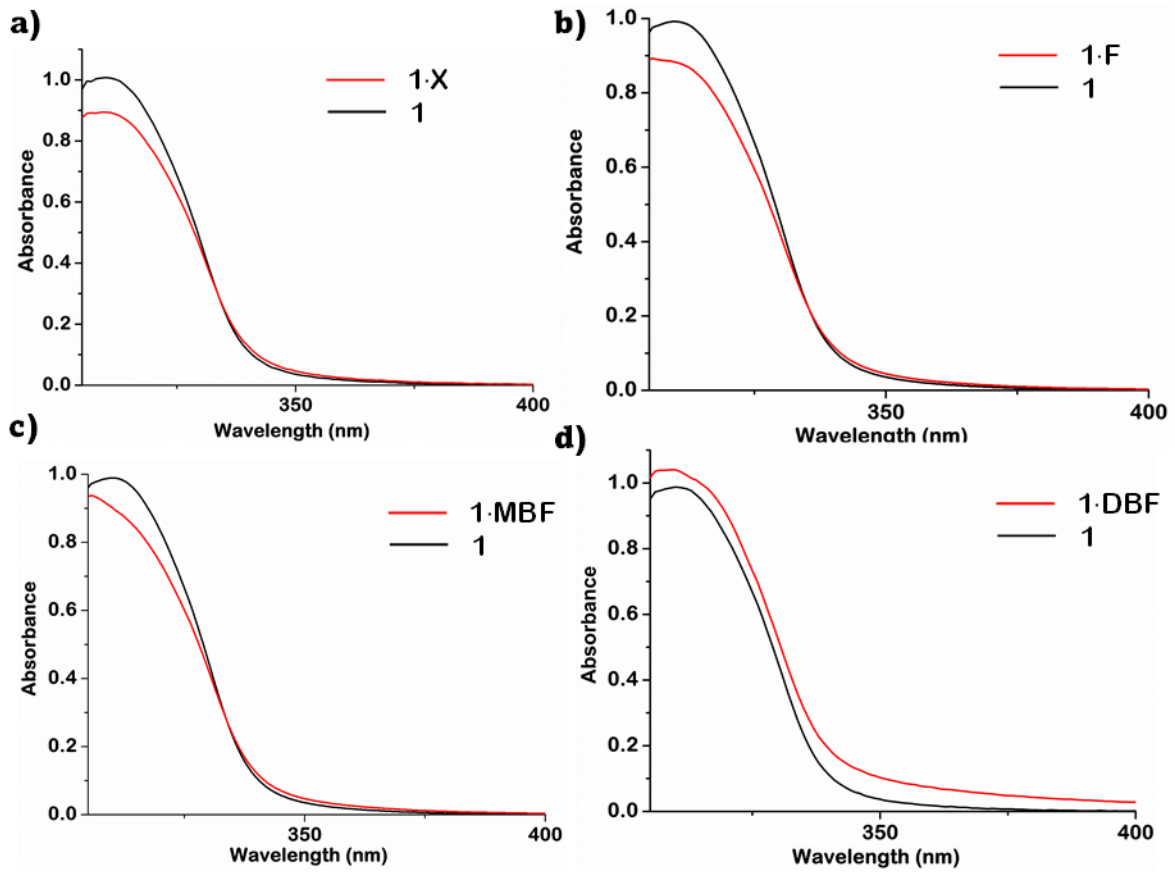


Fig. S35: UV-Vis spectra in water a) cage **1** with xanthene, b) cage **1** with fluorene, c) cage **1** with 2-bromofluorene, and d) cage **1** with 2,7-dibromofluorene.

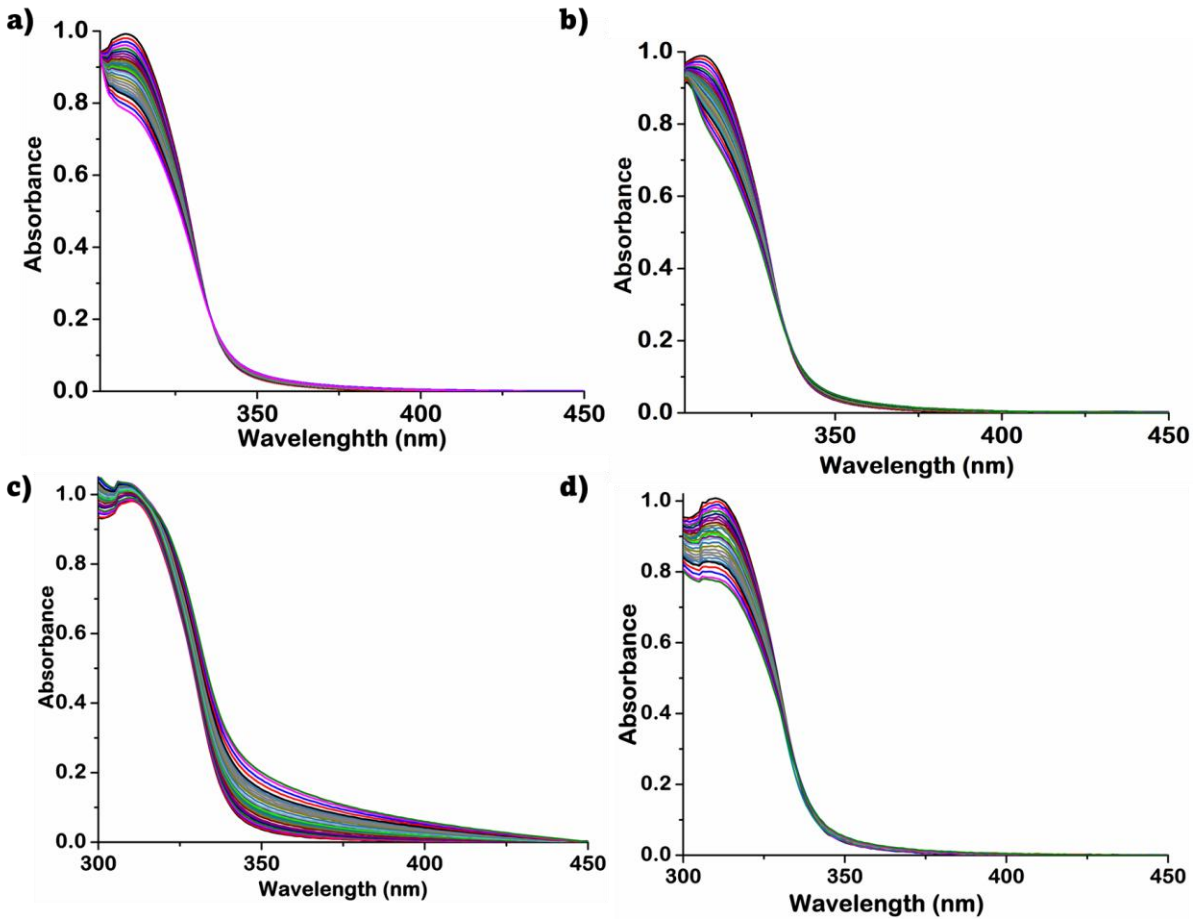


Fig. S36: UV-Vis titration of **1** (2 ×10^{-5} M in H_2O) with a) fluorene (0-3 equivalent), b) 2-bromofluorene (0-3 equivalent), c) 2,7-dibromofluorene (0-3 equivalent), and d) xanthene (0-3 equivalent).

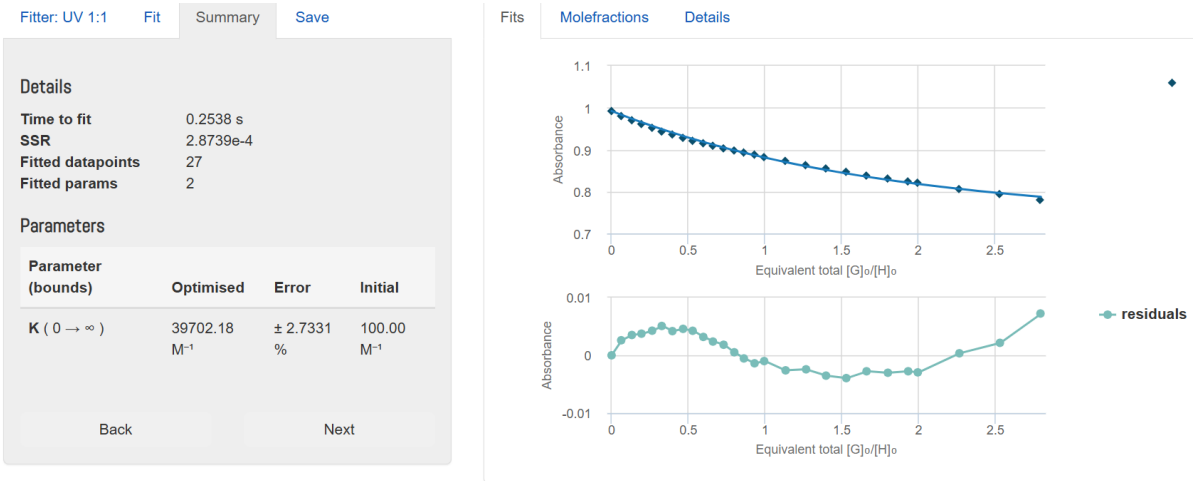


Fig. S37: Binding constant calculation of the host-guest complex of **1** with fluorene by using bindfit software (K_a = 3.97×10^4 M^{-1}).

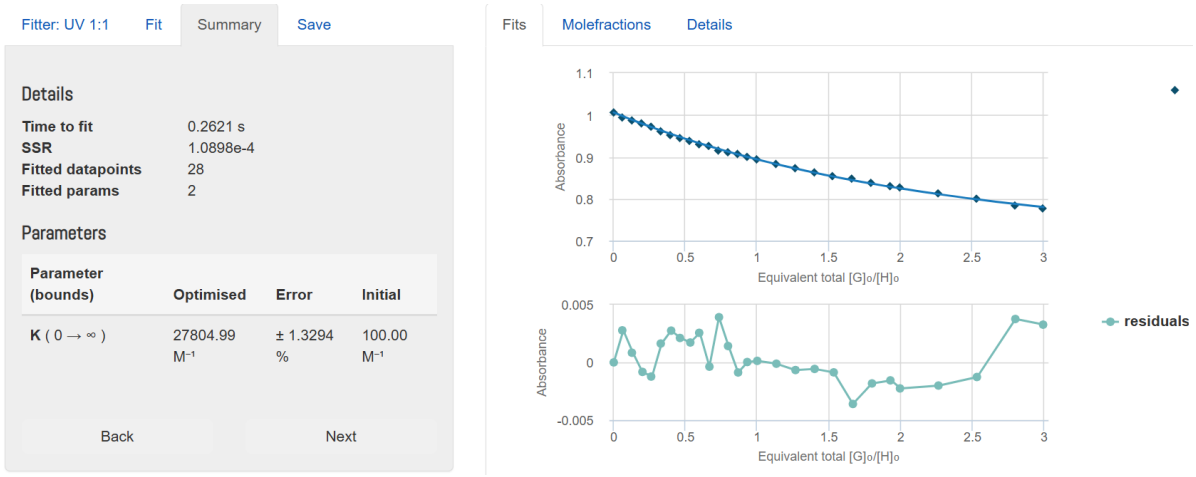


Fig. S38: Binding constant calculation of the host-guest complex of **1** with 2-bromofluorene by using bindfit software ($K_a = 2.78\times10^4\ M^{-1}$).

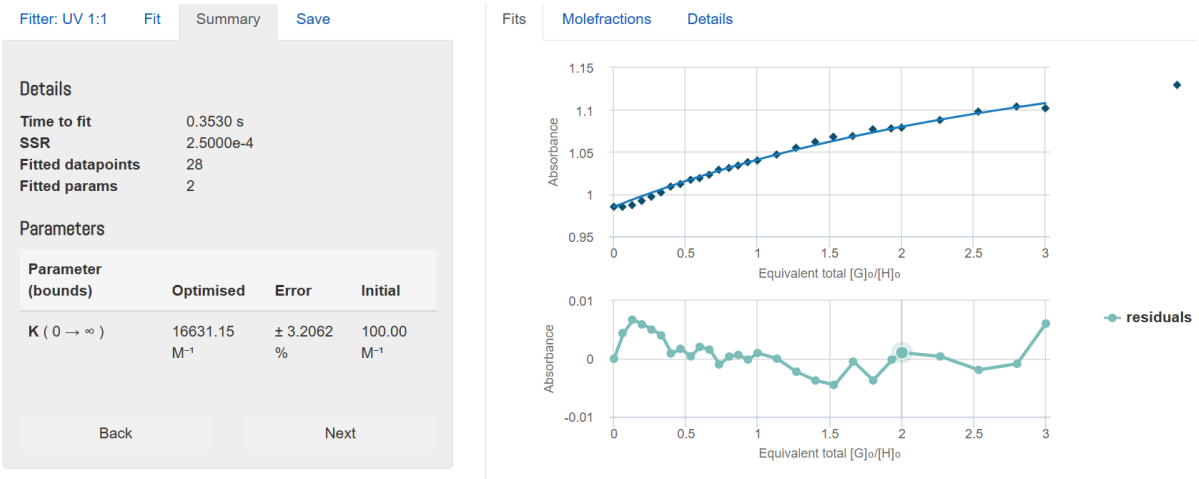


Fig. S39: Binding constant calculation of the host-guest complex of **1** with 2,7-dibromofluorene by using bindfit software ($K_a = 1.66\times10^4\ M^{-1}$).

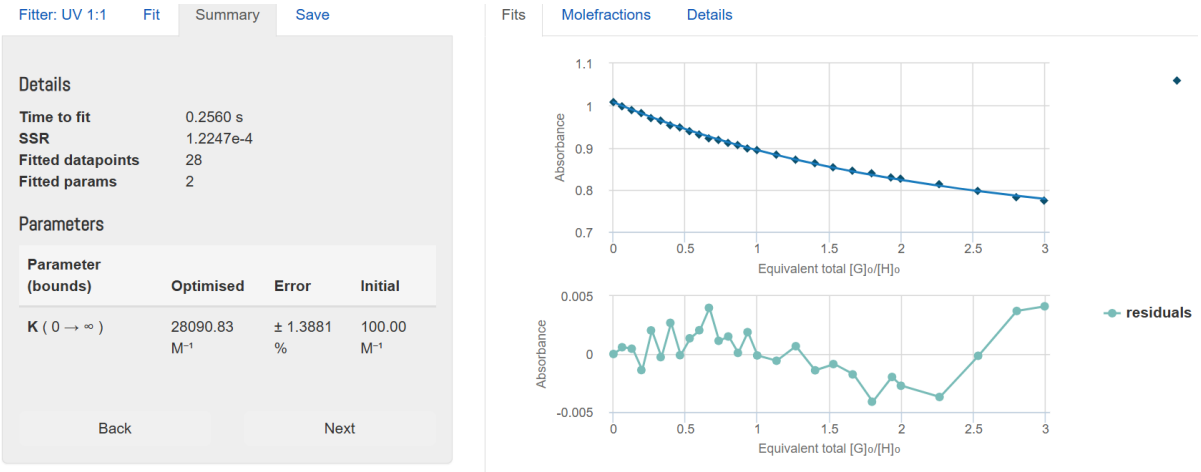


Fig. S40: Binding constant calculation of the host-guest complex of **1** with xanthene by using bindfit software ($K_a = 2.80\times10^4\ M^{-1}$).

7. Selective host-guest extraction experiment and oxidation:

7.1 Selectivity between fluorene and 2-bromofluorene

The selectivity of the guest molecules (fluorene and 2-bromofluorene) inside **1** was probed by taking a 0.5 mL of aqueous solution of the cage in a 4 mL glass vial. Then solid guests were added in equimolar ratio and stirred the reaction at 50 °C for 10 h. The host-guest complex was centrifuged to remove the excess guest molecules, and a clear supernatant was used for the oxidation. The reaction mixture was then stirred in the presence of white light (100 W 390 nm LED) for 10 hours at room temperature. After the completion of the reaction, 0.5 mL of $CDCl_3$ was added to it, and the mixture was stirred for 15-20 minutes and the ^1H NMR of the $CDCl_3$ extract of the product was recorded.

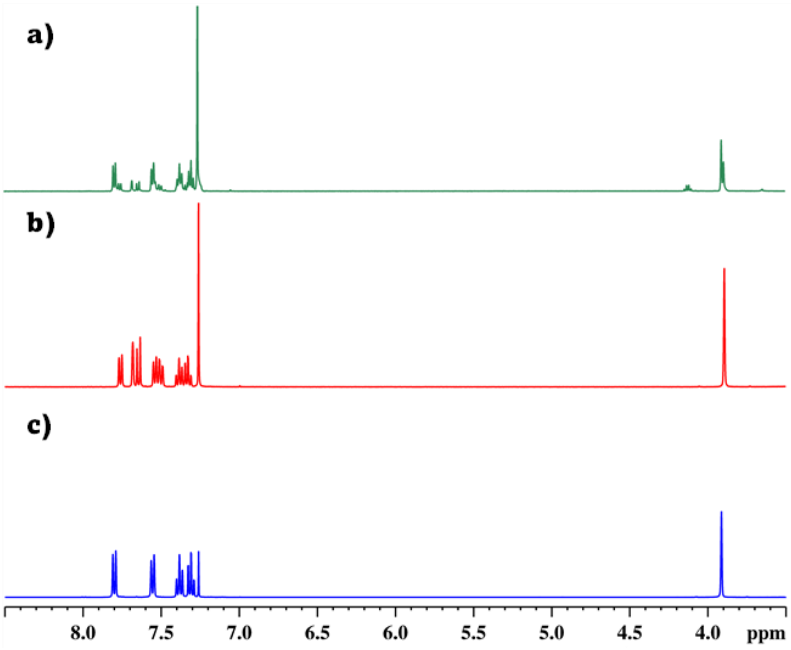


Fig. S41: Partial ^1H NMR (in $CDCl_3$) stack plot of a) the guest extracted from the supernatant upon treating an equimolar mixture of the fluorene and 2-bromofluorene with cage **1** in water, b) ^1H NMR of the 2-bromofluorene in $CDCl_3$, and c) ^1H NMR of the fluorene in $CDCl_3$.

7.2 Selectivity between fluorene and 2,7-dibromofluorene

The selectivity of the guest molecules (fluorene and 2,7-dibromofluorene) inside **1** was probed by taking a 0.5 mL of aqueous solution of the cage in a 4 mL glass vial. Solid guests were added in the equimolar ratio and stirred the reaction at 50 °C for 10 h. The host-guest complex was centrifuged to remove the excess guest molecules, and a clear supernatant was used for the oxidation. The reaction was then stirred in the presence of white light (100 W 390 nm LED) for 10 hours at room temperature. After the completion of the reaction, 0.5 mL of $CDCl_3$ was added to it, and the reaction was stirred for 15-20 minutes and the ^1H NMR of the product was recorded.

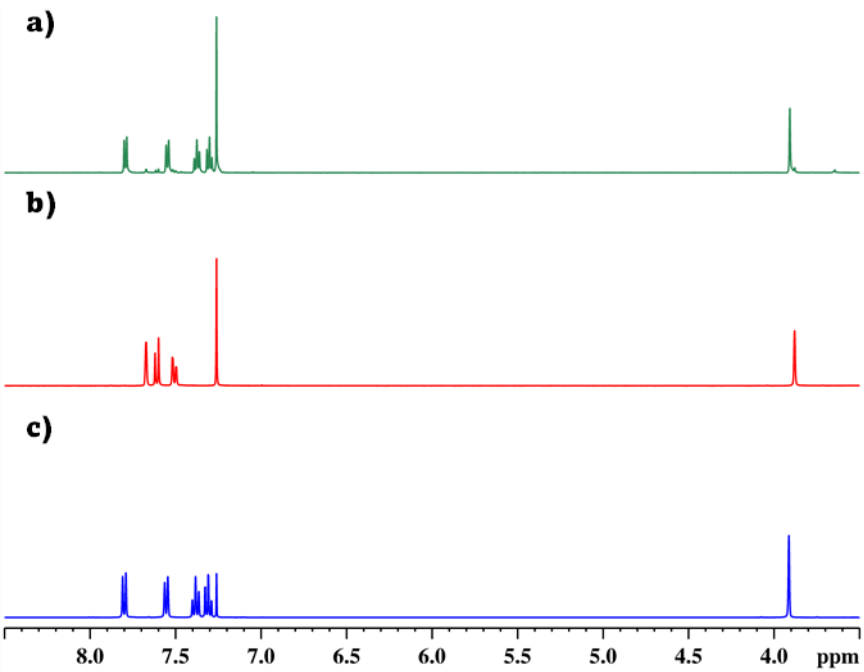


Fig. S42: Partial ^{1}H (in $CDCl_3$) stack plot of a) the guest extracted from the supernatant upon treating an equimolar mixture of fluorene and 2,7-dibromofluorene with **1** in water, b) ^{1}H NMR of the 2,7-dibromofluorene in $CDCl_3$, and c) ^{1}H NMR of the fluorene in $CDCl_3$.

7.3 Selectivity between 2-bromofluorene and 2,7-dibromofluorene

The selectivity of the guest molecules (2-bromofluorene and 2,7-dibromofluorene) inside **1** was probed by taking a 0.5 mL of aqueous solution of the cage in a 4 mL glass vial. And then solid guests were added in the equimolar ratio and stirred the reaction at 50 °C for 10 h. The host-guest complex was centrifuged to remove the excess guest molecules, and a clear supernatant was used for the oxidation. The reaction was then stirred in the presence of white light (100 W 390 nm LED) for 10 hours at room temperature. After the completion of the reaction, 0.5 mL of $CDCl_3$ was added to it, and the reaction was stirred for 15-20 minutes and the ^{1}H NMR of the product was recorded.

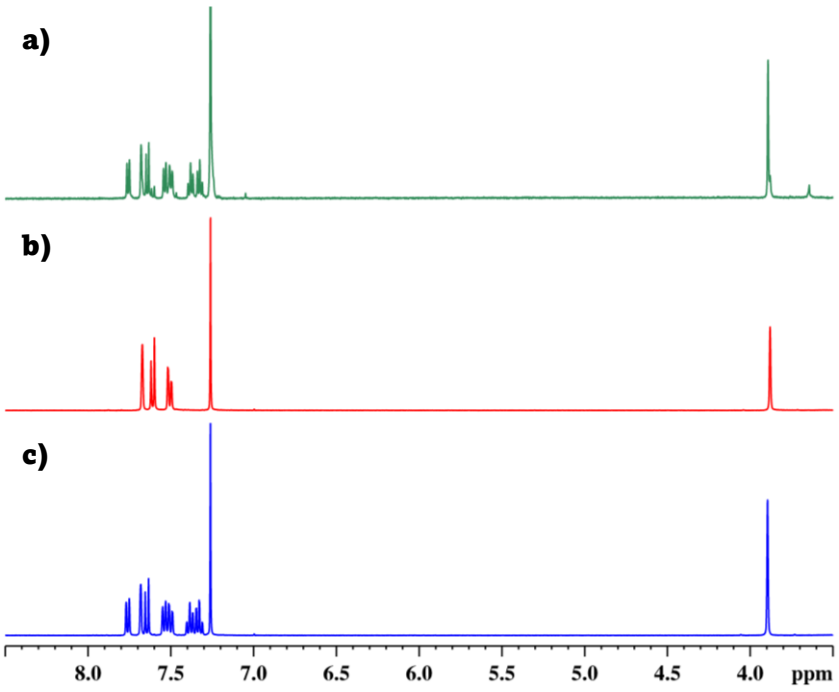


Fig. S43: Partial ^{1}H stack plot of a) the guest extracted from an equimolar mixture of the 2-bromofluorene and 2,7-dibromofluorene from **1** in $CDCl_3$. b) ^{1}H NMR of the 2,7-dibromofluorene in $CDCl_3$, and c) ^{1}H NMR of the 2-bromofluorene in $CDCl_3$.

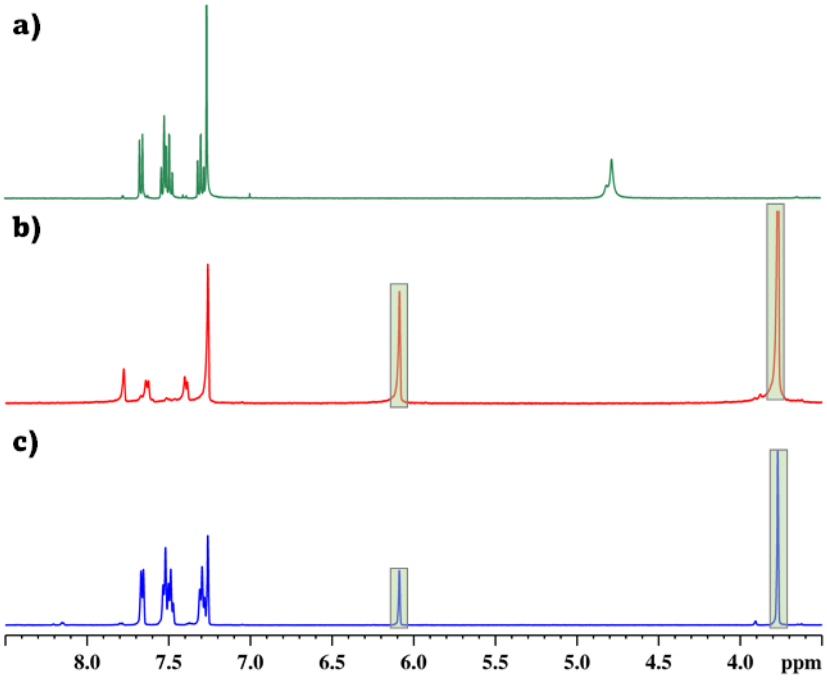


Fig. S44: Partial ^{1}H NMR stack (in $CDCl_3$) plot of the a) upon oxidation of fluorene from an equimolar mixture of the fluorene and 2,7-dibromofluorene in presence of **1** in aqueous medium, b) ^{1}H NMR of the 2,7-dibromofluorenone in $CDCl_3$, and c) ^{1}H NMR of the fluorenone in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

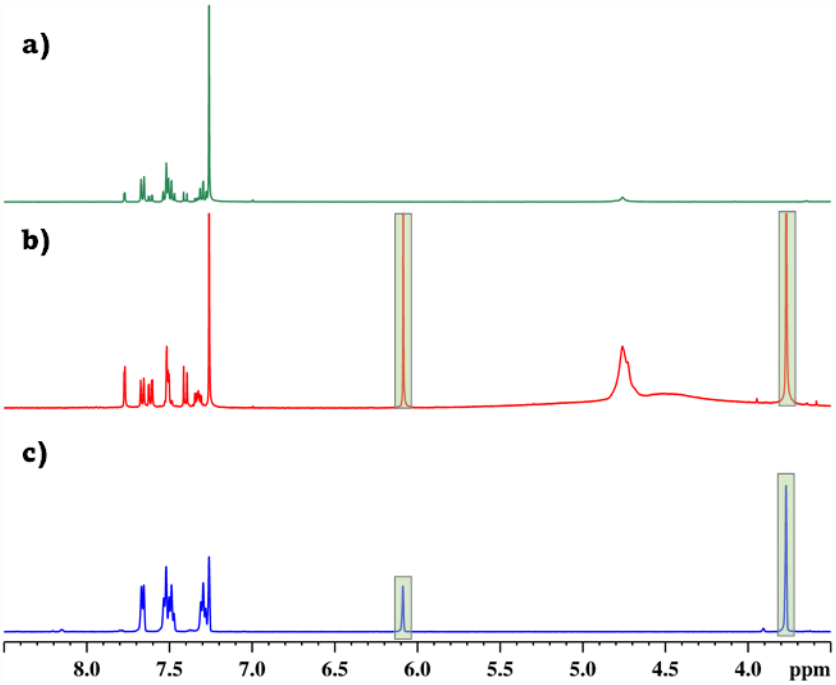


Fig. S45: Partial ^{1}H NMR stack (in $CDCl_3$) plot of the a) selective oxidation of fluorene from an equimolar mixture of the fluorene and 2-bromofluorene in presence of **1** in aqueous medium, b) ^{1}H NMR of the 2-bromofluorenone in $CDCl_3$, and c) ^{1}H NMR of the fluorenone in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

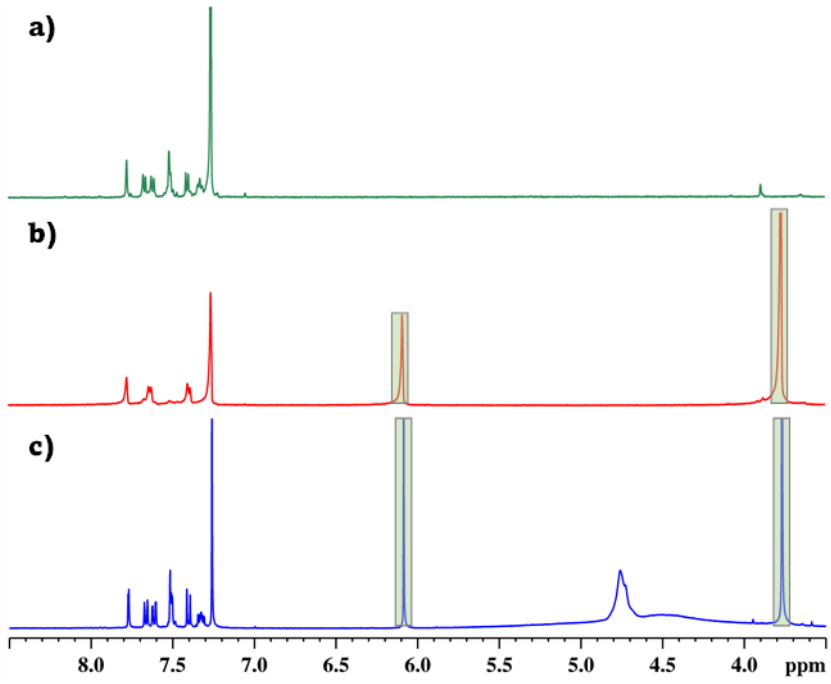


Fig. S46: Partial ^{1}H NMR stack plot of the a) selective oxidation of 2-bromofluorene from an equimolar mixture of the 2-bromofluorene and 2,7-dibromofluorene inside **1** in $CDCl_3$, b) ^{1}H NMR of the 2,7-dibromofluorenone in aqueous medium, and c) ^{1}H NMR of the 2-

bromofluorenone in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

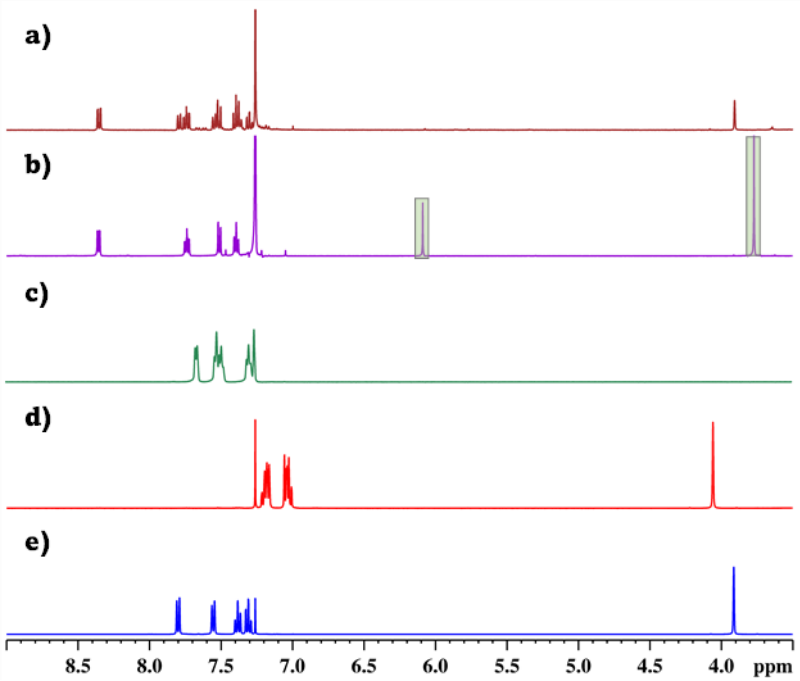


Fig. S47: Partial ^1H NMR (in $CDCl_3$) stack plot of the a) extracted product from an equimolar mixture of the xanthene and fluorene in presence of **1** in aqueous medium (under the white LED), b) ^1H NMR of the xanthone in $CDCl_3$, c) ^1H NMR of the fluorenone in $CDCl_3$, d) ^1H NMR of the xanthene in $CDCl_3$, and e) ^1H NMR of the fluorene in $CDCl_3$. Peaks for the internal standard (1,3,5-Trimethoxybenzene) are highlighted in green.

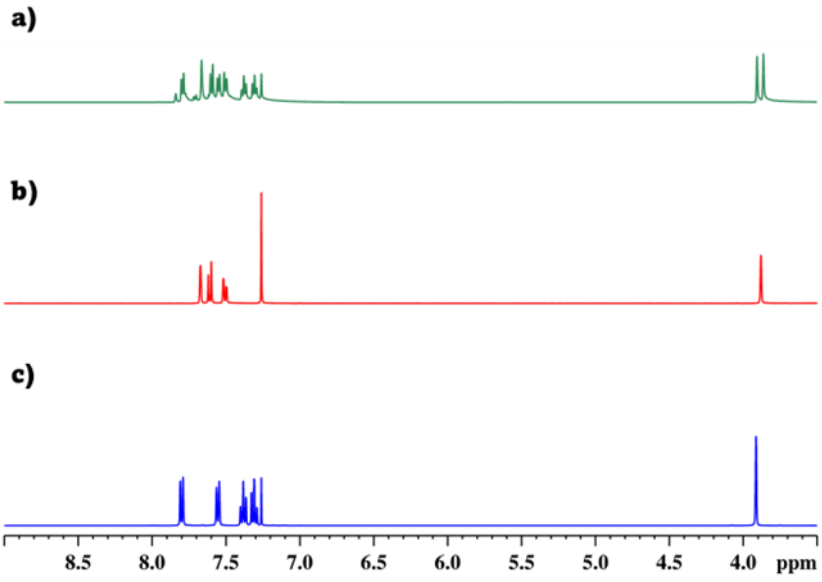


Fig. S48: Partial ^{1}H NMR (in $CDCl_3$) stack plot of the a) extracted product of the blank reaction of a mixture of fluorene with 2,7-dibromofluorene in acetone under 390 nm LED without cage, b) ^{1}H NMR of the 2,7-dibromofluorene in $CDCl_3$, c) ^{1}H NMR of the fluorene in $CDCl_3$.

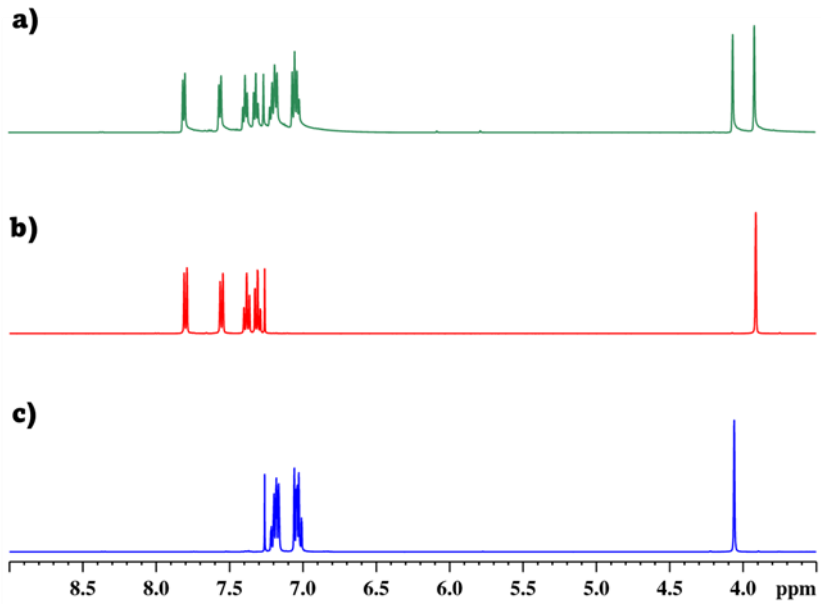


Fig. S49: Partial ^{1}H NMR (in $CDCl_3$) stack plot of the a) extracted product of the blank reaction of a mixture of fluorene and xanthene in acetone under white led without cage, b) ^{1}H NMR of the fluorene in $CDCl_3$, c) ^{1}H NMR of the xanthene in $CDCl_3$. In this no oxidation was observed.

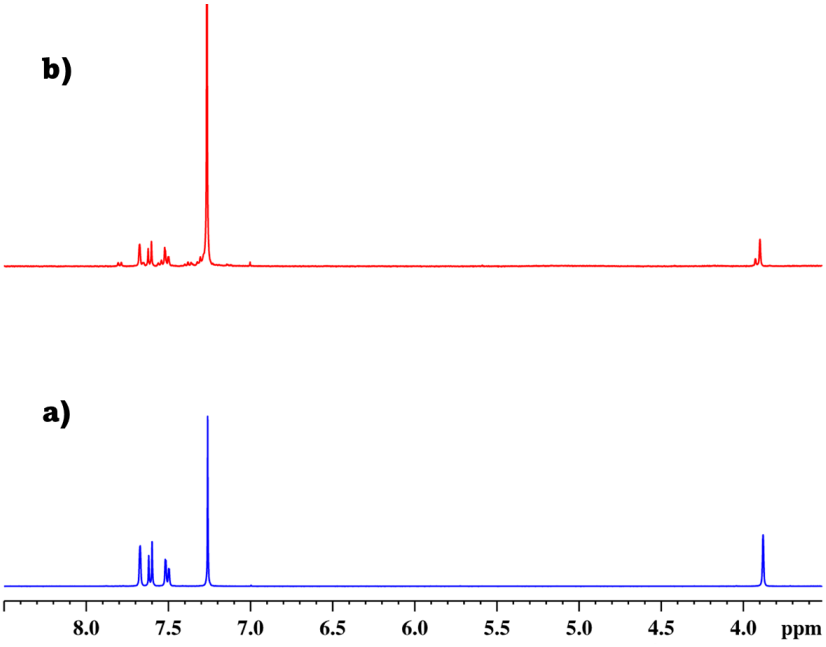


Fig. S50: Partial ^{1}H NMR stack plot of a) 2,7-dibromofluorene in $CDCl_3$, and b) the solid left behind after centrifuging the solution of the reaction of a mixture of fluorene and 2,7-dibromofluorene in presence of **1** in water.

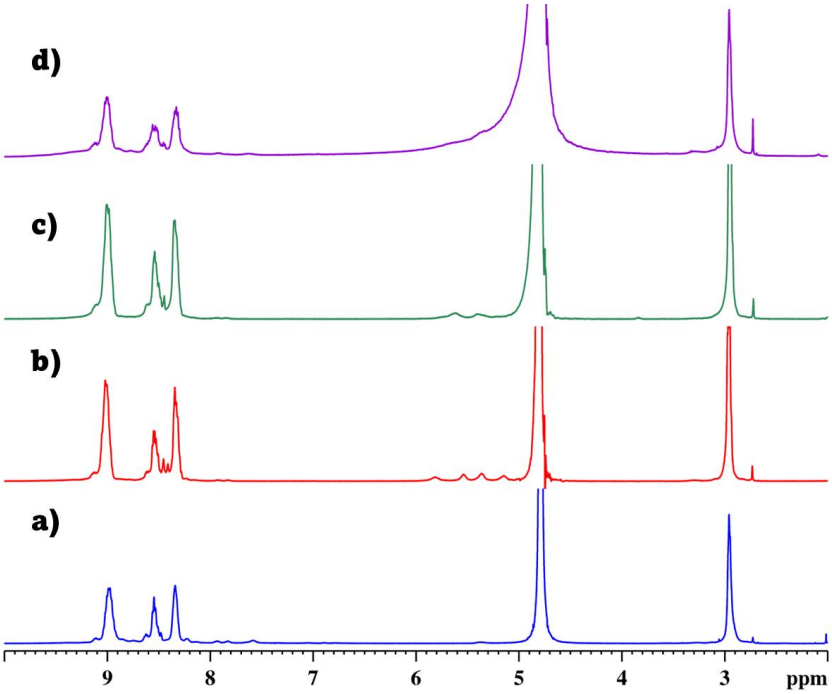


Fig. S51: The ^{1}H NMR stack plot of a) **1** in D_2O, b) **1⊃Fluorene** in D_2O, c) **1⊃Fluorene** in D_2O after 100 W 390 irradiation for 10 h, and d) **1** in D_2O after extraction of the product.

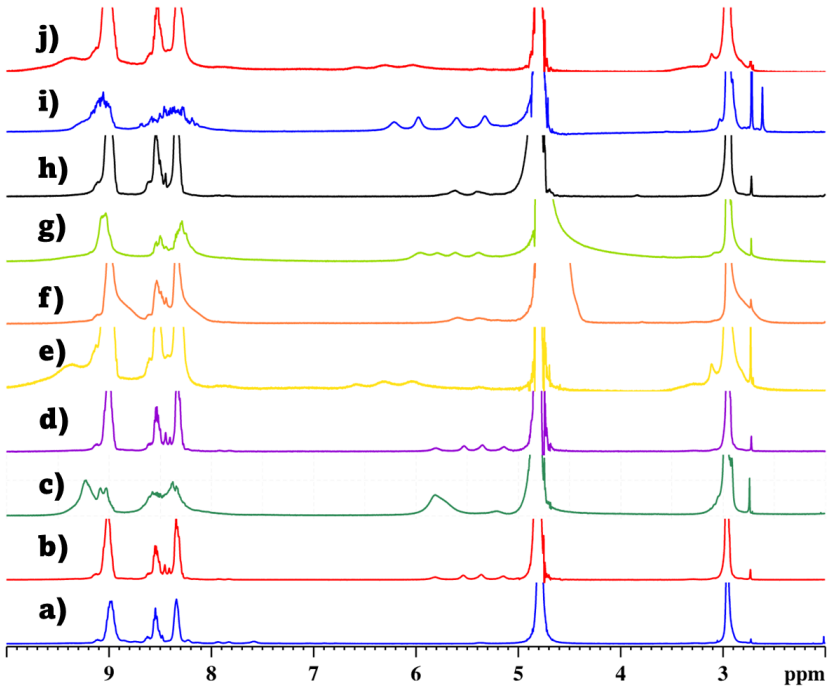


Fig. S52: The ^{1}H stack plot of a) **1** in D_2O, b) **1⊃Fluorene**, c) **1⊃Thioxanthene** in D_2O, d) **1⊃2-bromofluorene** in D_2O, e) **1⊃2,7-dibromofluorene** in D_2O, f) **1⊃9,10-dihydroacridine** in D_2O, g) **1⊃10-methyl-9,10-dihydroacridine,** h) **1⊃10-ethyl-9,10-dihydroacridine** in D_2O, i) **1⊃Xanthene**, in D_2O, and j) **⊃10-propyl-9,10-dihydroacridine,** in D_2O.

8. Calculation of Hydrodynamic Radius from DOSY experiment:

The ^{1}H DOSY NMR spectrum for **1** was recorded, and the corresponding hydrodynamic radius (r) was calculated from the diffusion coefficient (D) value using the Stokes-Einstein equation:

$$r = k_B T / 6\pi\eta D$$

[where r: hydrodynamic radius; D: diffusion coefficient; η: coefficient of viscosity; k_B: Boltzmann constant; T: temperature in Kelvin scale].

(Diffusion Coefficient = 1.62 x 10^{-10} m^2s); (T = 298 K); (Solvent = D_2O); The coefficient of viscosity of D_2O at 298 K, η = 1.107 centipoise; Boltzmann constant (kB) = 1.38 x 10^{-23} $m^2kgs^{-2}K^{-1}$.

$$r = 12.17 \text{ Å}$$

The hydrodynamic radius was compared with the single crystal structure of cage **2** and the optimized structure of cage **1**.

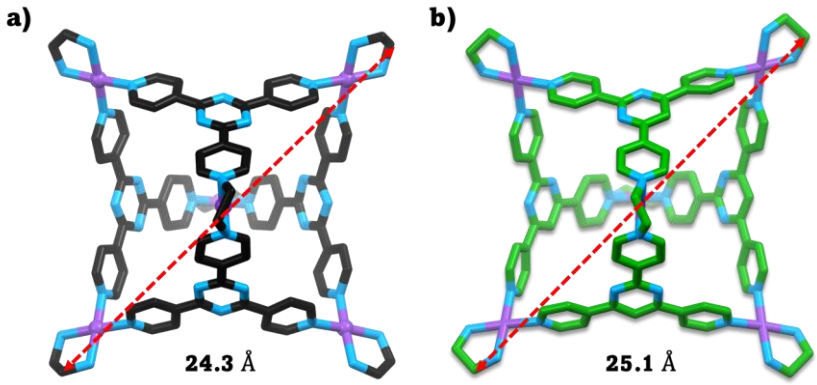


Fig. S53: a) single crystal structure of **2**, b) DFT-optimized structure of **1**.

9. Computational Studies:

Full geometry optimizations were carried out using the *Gaussian 09* package. The hybrid B3LYP functional has been used in the calculations of cage **1**, as implemented in the *Gaussian 09* package.[1] The LanL2DZ basis set was used in the case of the palladium atom and the 6-31g(d) basis set for all other atoms in all calculations.

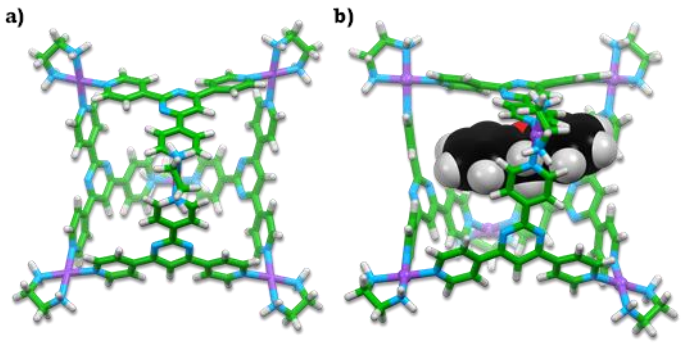


Fig. S54: Optimized structure of a) **1** and b) **X⊂1**.

Table S1: The Energy calculations of **1**, **2**, and **3** and their host-guest inclusion complexes with model guest (Xanthene) were calculated using the PM6 optimized structure. The energy values are given in Table S1.

Sr. No.	Molecule	Solvent	Zero-point energy (Hartree)	Host-guest stabilization energy (Hartree)
1	**1**	Water	8.947714	
2	**2**	Water	6.774224	
3	**3**	Water	3.257855	
4	**X⊂1**	Water	2.598919	-6.358748
5	**X⊂2**	Water	3.020664	-3.763513
6	**X⊂3**	Water	3.071682	-0.196126
7	**X**	Water	0.009953	

Coordinates of 1

Pd	-1.73589	-0.17739	-8.01842
Pd	1.01303	-8.90305	-0.16845
Pd	9.22931	0.8517	-1.39412
Pd	-1.1483	9.06304	-0.03452
C	-2.83412	7.06757	0.27954
H	-2.7244	7.32915	1.34102
C	-3.54697	5.93333	-0.10783
H	-3.9876	5.28225	0.65188
C	-3.6589	5.64526	-1.46812
C	-3.08973	6.53983	-2.37709
H	-3.17558	6.37784	-3.45575
C	-2.38127	7.63735	-1.8792
H	-1.88774	8.34382	-2.56587
N	-2.22956	7.89572	-0.57376
C	-4.28866	4.37716	-1.90589
C	-5.27753	3.721	-1.15777
H	-5.71761	4.1872	-0.27439
C	-5.66839	2.4391	-1.57297
N	-5.14925	1.87488	-2.69598
C	-4.24744	2.60046	-3.41429
N	-3.78956	3.83201	-3.04876
C	-6.60323	1.59048	-0.80169

C	-6.76442	1.78296	0.56693
H	-6.25033	2.5898	1.09598
C	-7.58295	0.90501	1.27089
H	-7.73507	1.01989	2.35275
N	-8.21373	-0.13093	0.7209
C	-8.08449	-0.28399	-0.59985
H	-8.62852	-1.1389	-1.03262
C	-7.30241	0.54502	-1.40362
H	-7.22718	0.36143	-2.48002
C	-3.68269	1.97879	-4.63521
C	-2.47399	2.42897	-5.15538
H	-1.94915	3.27709	-4.70875
C	-1.93432	1.76972	-6.25692
H	-0.98171	2.09249	-6.69706
N	-2.49808	0.71758	-6.84295
C	-3.67847	0.31322	-6.35828
H	-4.12786	-0.55349	-6.86867
C	-4.31694	0.91046	-5.26966
H	-5.28338	0.53541	-4.91835
C	7.34073	-0.96034	-1.0974
H	7.72066	-0.9767	-0.06732
C	6.20911	-1.68898	-1.45522
H	5.66711	-2.2756	-0.70798
C	5.77853	-1.63924	-2.7781
C	6.5238	-0.89046	-3.68878
H	6.25289	-0.84587	-4.74696
C	7.63106	-0.17962	-3.21498
H	8.22226	0.45555	-3.89334
N	8.03246	-0.19303	-1.93801
C	4.53195	-2.32916	-3.18202
C	3.60648	-1.6877	-4.0135
H	3.78747	-0.67218	-4.36901
C	2.43896	-2.37645	-4.35407
N	2.18597	-3.60626	-3.84393
C	3.11495	-4.1559	-3.0145
N	4.30376	-3.57272	-2.68676
C	1.41434	-1.8128	-5.25968
C	1.73437	-0.85697	-6.22212
H	2.75562	-0.48676	-6.34365
C	0.71537	-0.36847	-7.04226
H	0.92547	0.41126	-7.79188
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H	12.63488	2.15317	-1.5382
H	11.39417	2.04698	-2.81126
C	11.76448	0.19383	-1.70811
H	12.65119	-0.16177	-2.28124
H	11.91932	-0.17912	-0.66281
N	10.46927	-0.26861	-2.19287
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C	-2.42252	0.14597	-10.53801
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H	-3.1379	0.24585	-11.38698
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H	-1.63854	-1.67047	-11.36897
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Pd	-9.06844	-1.23906	1.63422
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H	0.34791	7.30363	-1.49181
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H	2.00578	5.52917	-0.85794
C	1.8935	6.02143	1.25594
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H	-0.18175	8.46147	2.42237
N	0.01975	7.94459	0.4275

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C	6.01783	3.08979	0.78731
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H	5.60867	4.01594	-1.14019
C	7.3213	2.70067	-1.18814
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N	8.13126	1.83761	-0.57806
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H	6.79858	2.04707	2.52894
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H	3.81093	-0.23422	6.22938
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C	-5.14529	-3.00144	2.95596
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C	-1.23945	-5.8219	2.22368
C	-1.66554	-6.18251	0.94768
H	-2.52881	-5.69839	0.48139
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H	-1.25161	-7.47866	-0.74862
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H	-12.73225	-0.78802	1.51312
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C	-11.3463	-2.39333	1.88691
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C	2.44219	-0.46517	10.54125
H	2.20998	-0.72653	11.5997
H	3.34292	-1.07628	10.2756
N	1.3862	-0.7365	9.57277
H	-0.87707	-10.03218	0.86334
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H	2.99663	-9.96224	-1.07811
H	1.71755	-10.20777	-2.09816
H	-10.57839	0.68038	1.3821
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H	-10.12976	-2.20646	3.54222
H	-9.68073	-3.40698	2.49557
H	10.30052	2.98599	-0.99392
H	10.82672	1.85643	0.09516
H	10.43661	-0.23184	-3.21843
H	10.33157	-1.24813	-1.91676
H	0.48417	-0.39293	9.9276
H	1.29807	-1.75028	9.44408
H	3.06811	2.17401	8.78805
H	4.01969	0.82645	8.87101
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Coordinates of X⊂1

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Pd	-0.47196	-9.25455	-0.66376
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H	2.32745	7.54338	-0.44338
C	3.03211	5.96994	0.90864
H	3.55443	5.42235	0.11925
C	3.03046	5.51696	2.23869
C	2.33635	6.26366	3.20773
H	2.32416	5.95101	4.25684
C	1.63963	7.41469	2.81427
H	1.05792	8.01103	3.54045
N	1.63035	7.84951	1.51991
C	3.71826	4.25461	2.61577
C	4.8476	3.76521	1.92707
H	5.29644	4.33624	1.11046
C	5.38322	2.52246	2.32599
N	4.85771	1.84222	3.39372
C	3.77671	2.38794	4.04141
N	3.17688	3.56615	3.66823
C	6.49411	1.85753	1.60221
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C	7.91999	1.63829	-0.31783
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N	8.4505	0.49201	0.15176
C	8.0503	0.0436	1.36024
H	8.5299	-0.88026	1.7246
C	7.08097	0.6987	2.10891
H	6.77898	0.29207	3.07839
C	3.2045	1.65183	5.20362
C	2.18918	2.23219	5.98857
H	1.81423	3.23879	5.77428
C	1.64896	1.50125	7.05887
H	0.84453	1.91616	7.69377
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C	3.08857	-0.30748	6.62745
H	3.432	-1.31304	6.93037
C	3.66296	0.36259	5.53461
H	4.45612	-0.12299	4.95569
C	-7.55409	-1.7275	0.96628
H	-7.91689	-1.75962	-0.07574

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H	-5.81909	-2.97721	0.61435
C	-5.98199	-2.35196	2.69724
C	-6.76702	-1.63458	3.61434
H	-6.50618	-1.58992	4.67536
C	-7.90229	-0.95298	3.15421
H	-8.52477	-0.34675	3.83631
N	-8.28532	-0.98444	1.84649
C	-4.71401	-2.99581	3.12938
C	-3.92564	-2.44465	4.16339
H	-4.23873	-1.53137	4.67822
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C	-1.82086	-2.59679	5.58377
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H	-3.11599	-0.94293	6.18931
C	-1.28482	-1.00406	7.33122
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C	-2.4153	-7.07398	-0.03558
H	-2.69695	-7.26089	-1.08674
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C	-1.12697	-7.74026	1.80589
H	-0.36863	-8.43849	2.20332
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C	1.39205	-1.72775	11.58456
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C	-6.77297	3.08998	0.49687
H	-6.22855	3.80168	1.1233
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C	5.59287	-2.35638	-2.86313
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C	3.51705	-1.92719	-4.24701
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N	11.43246	0.19743	-0.08825
C	12.56139	-0.28135	-0.95299
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H	-1.11718	-11.21084	1.04641
H	11.4276	1.22163	-0.04128
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H	3.49456	-0.41074	10.22264
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H	0.05498	-2.76158	10.35465
H	-0.52533	-1.30377	10.85237
H	2.8365	10.63403	1.45336
H	1.89958	10.84166	2.79141
H	-0.76969	11.36768	-0.40942
H	-1.74494	10.98369	0.86013
C	3.24929	2.21	-3.30529
C	1.88404	1.91697	-3.38328
C	1.33891	0.85644	-2.64449
C	2.21513	0.10233	-1.84538
C	3.58591	0.38204	-1.74438
C	4.09501	1.45196	-2.48412
C	-0.12767	0.55001	-2.6914
C	0.46785	-1.38141	-1.1684
C	-0.49202	-0.68327	-1.9211
C	-1.80531	-1.17579	-1.91557
H	-2.57668	-0.66117	-2.49219
C	-2.13368	-2.31754	-1.17765
C	-1.15339	-2.99364	-0.43922
C	0.16532	-2.53363	-0.42867
H	3.65828	3.03603	-3.88779
H	1.23466	2.51906	-4.02309
H	4.22648	-0.22326	-1.10508

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H	-3.16025	-2.68558	-1.17831
H	-1.4206	-3.884	0.13293
H	0.94296	-3.0461	0.13548
H	-0.70175	1.421	-2.2938
H	-0.46549	0.45343	-3.7507
O	1.80823	-0.9932	-1.07734

8. References

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