

Electronic Supplementary Information

Supramolecular Assemblies through Host-Guest Complexation between Cucurbiturils and an Amphiphilic Guest Molecule

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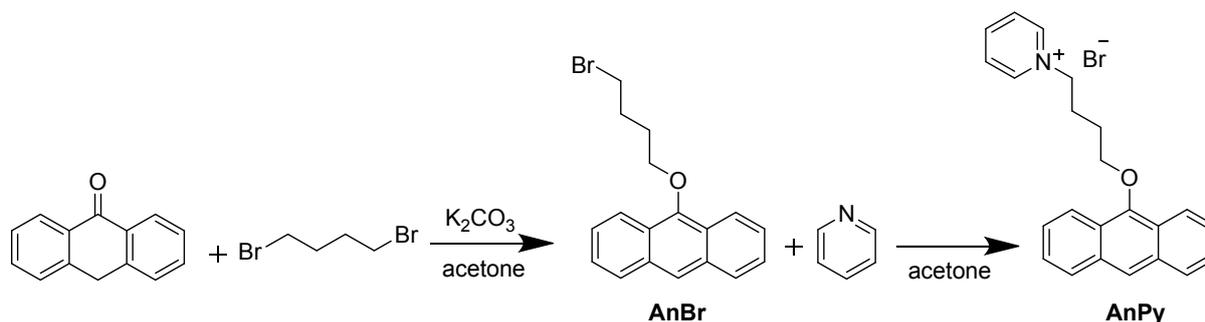
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1. Methods

Cucurbit[7]uril and cucurbit[8]uril were synthesized according to literature procedures.²⁻³ The CB8 sample contains traces of HCl from recrystallization, which enhances its water-solubility (up to 0.1 mM). NMR spectra were recorded on a JEOL JNM-ECX 400 spectrometer working at 400 MHz. Quantum-chemical calculations were performed with the Gaussian 09 package, utilizing density functional theory (DFT) with dispersion corrected method (wB97xd) in combination with 6-31G* basis set. ITC experiments were carried out on a VIP ITC from Microcal Inc. (Northampton, MA, United States) at 25 °C. The solutions were degassed and thermostated by a ThermoVac accessory for all experiments. The data was analyzed by Origin 7.0 software with the one set of sites model. UV-Vis absorption measurements were performed with a Varian Cary 4000 spectrophotometer and the fluorescence spectra were recorded on a Varian Cary Eclipse or a JASCO FP-8500 spectrofluorometer. All measurements were performed at ambient temperature, in rectangular SUPRASIL[®] quartz glass cuvettes (Hellma Analytics) with 1-cm optical path length. DLS and zeta potential measurements were performed on a Malvern Zetasizer Nano ZS instrument. TEM images were recorded with a Zeiss EM900 transmission electron microscope, in which the sample was put on the Cu-grid with carbon support film (carbon-film on 3.05 nm Cu-network 200 nm mesh) purchased from PLANO GmbH. An accelerating voltage of 80 kV was applied.

2. Synthesis and Characterization of AnPy

AnBr and AnPy were synthesized according to the literature (Scheme 1).¹



Scheme S1. Synthesis of AnBr and AnPy.

Synthesis of 9-(4-Bromobutoxy)anthracene (**AnBr**): 2.0 g (10.3 mmol) anthrone and 9.0 g (41.7 mmol) 1,4-dibromo butane, and 14.0 g (101.3 mmol) K_2CO_3 were mixed in 120 mL acetone under nitrogen atmosphere, and heated to reflux for 14 h (Scheme S1). After cooling to ambient temperature, the solvent was removed *via* rotary evaporation under reduced pressure, and the residue was purified by column chromatography (CH_2Cl_2 :petroleum ether = 1:10), giving 1.7 g (50% yield) of 9-(4-bromobutoxy)anthracene as a white solid.

Synthesis of **AnPy**: 360 mg (1.08 mmol) **AnBr** and pyridine (3 mL) were dissolved in acetone (100 mL), and the solution was heated to reflux for 48 h under nitrogen atmosphere (Scheme S1). After cooling to room temperature, the mixture was poured into diethyl ether (300 mL). The precipitated product was filtered and washed with diethyl ether. The product was dried overnight under vacuum, giving 250 mg (57% yield).

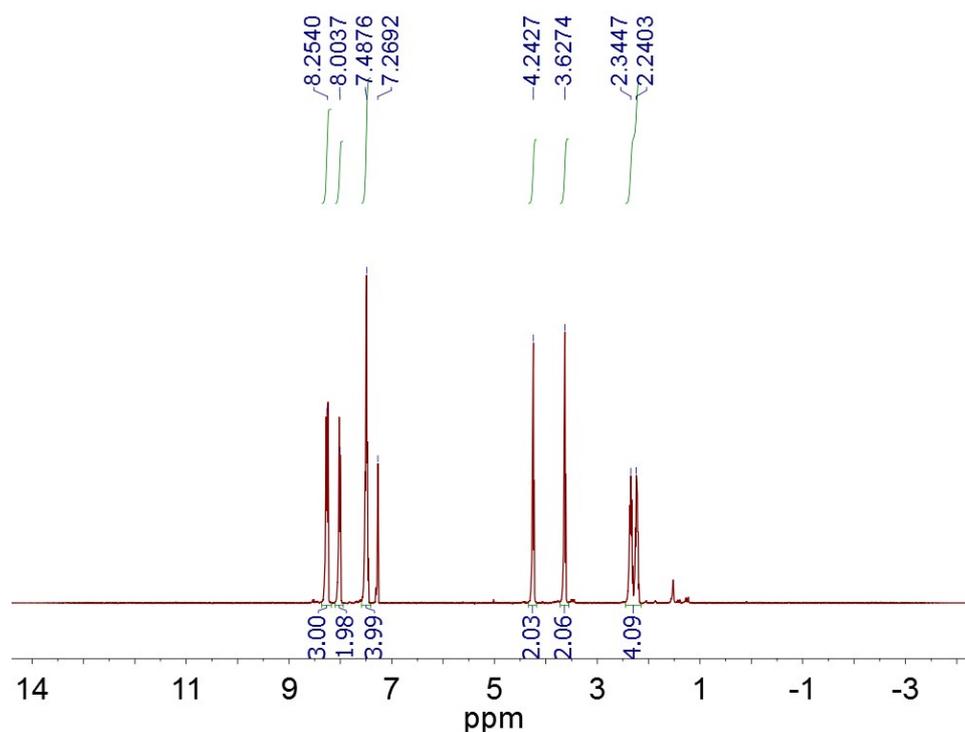


Figure S1. 1H NMR spectrum of AnBr in $CDCl_3$.

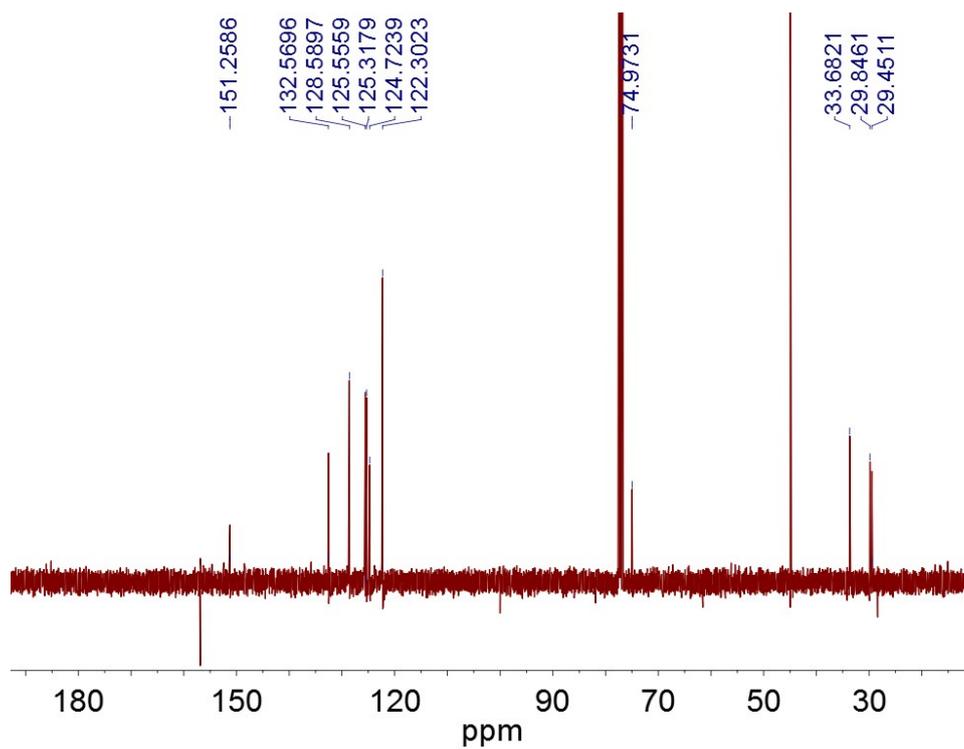


Figure S2. ^{13}C NMR spectrum of AnBr in CDCl_3 .

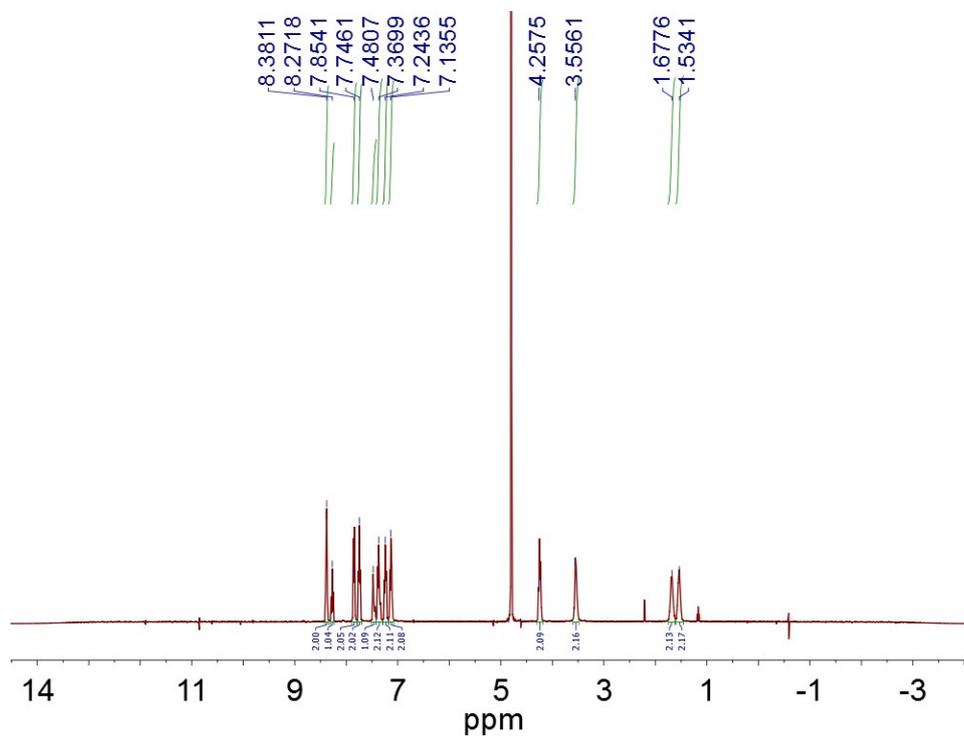


Figure S3. ^1H NMR spectrum of AnPy in D_2O .

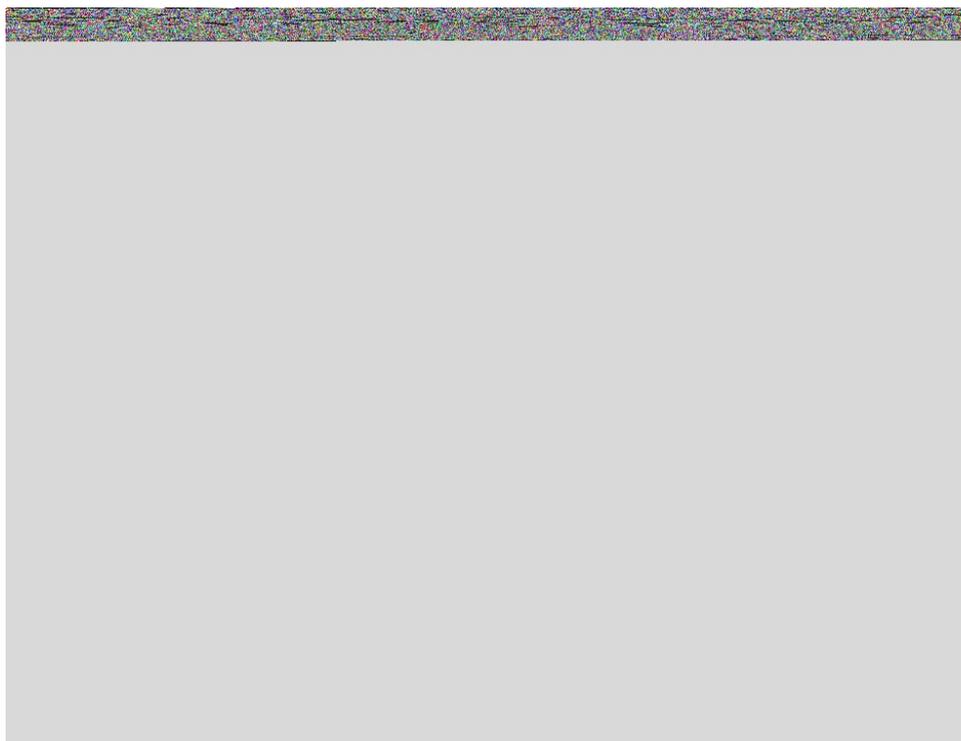


Figure S4. ^{13}C NMR spectrum of **AnPy** in D_2O .

3. Job's Plots of the $\text{CB}n\bullet\text{AnPy}$ Complexes

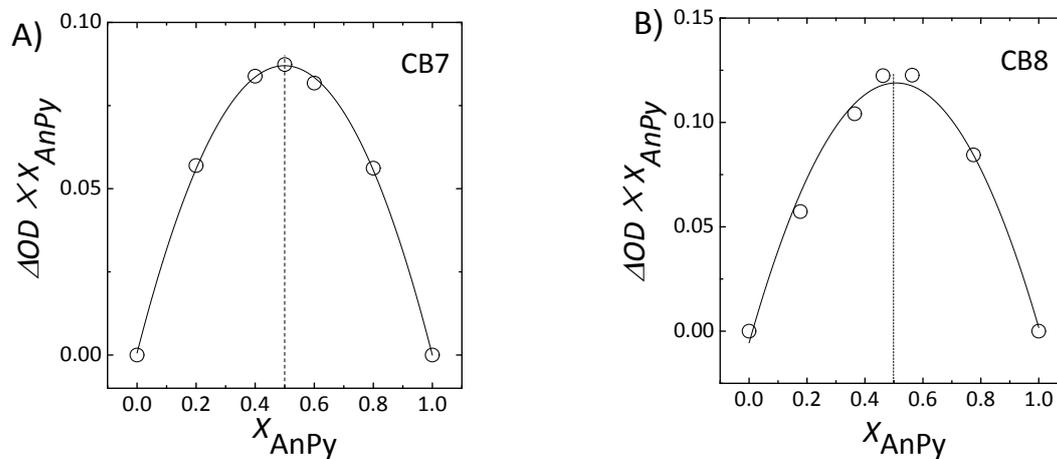


Figure S5. Job's plots for A) $\text{CB7}\bullet\text{AnPy}$ complex and B) $\text{CB8}\bullet\text{AnPy}$ complex.

4. ITC Experiments

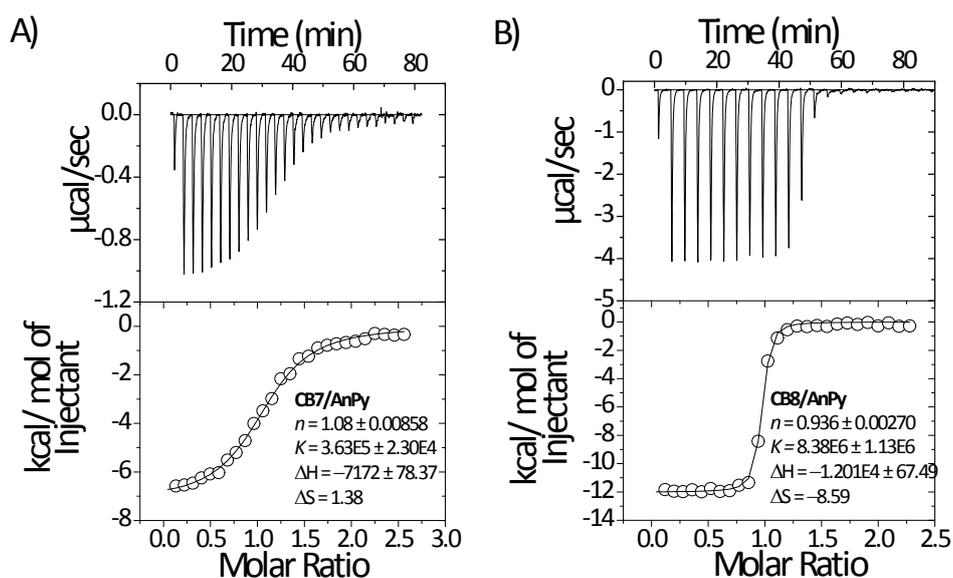


Figure S6. ITC isotherms for the titration of A) CB7 (0.5 mM) into a solution of 0.05 mM AnPy and B) AnPy (1.0 mM) into a solution of 0.10 mM CB8; experiments were done in water at 25 °C.

5. Competitive Titrations

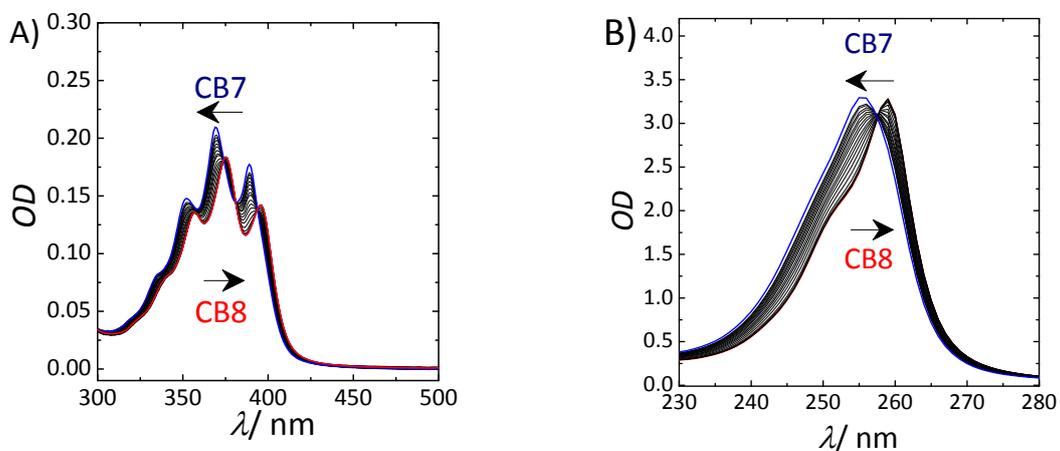


Figure S7. UV-Vis titrations of CB8•AnPy (35:35 µM) with CB7. A) UV-Vis change of the absorption bands of the anthracene (A) and the pyridinium residue (B).

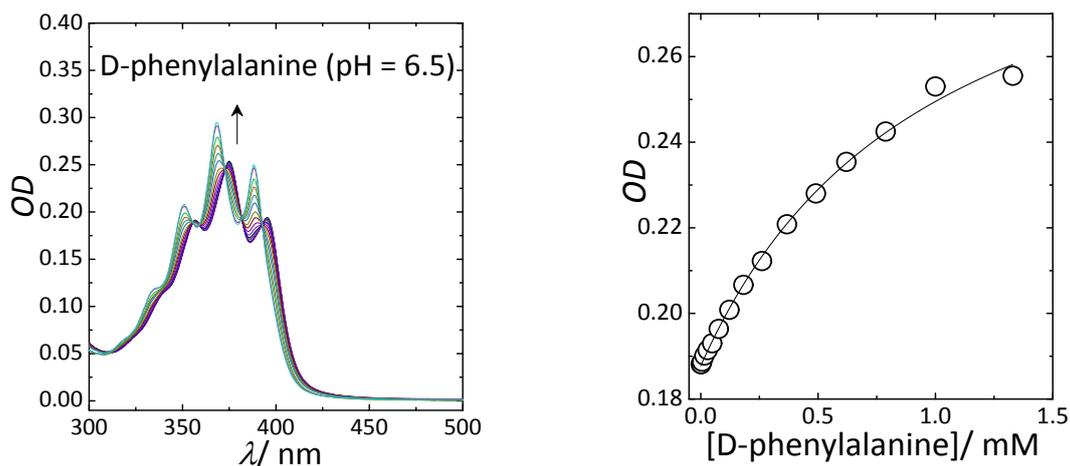


Figure S8. UV-Vis competitive titrations for the complexation of D-phenylalanine with the CB8•AnPy reporter pair (35:35 μM) at pH 6.5.

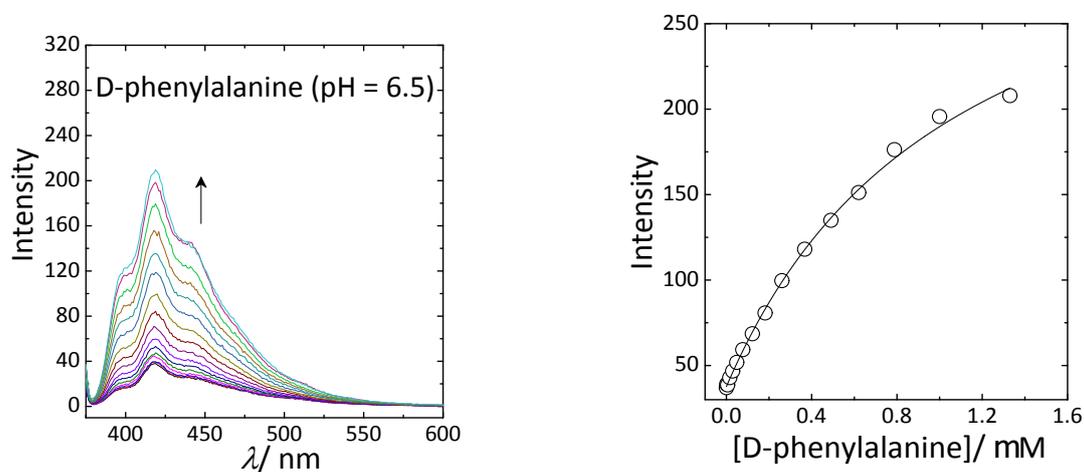


Figure S9. Fluorescence competitive titrations for the complexation of D-phenylalanine with the CB8•AnPy reporter pair (35:35 μM) at pH 6.5.

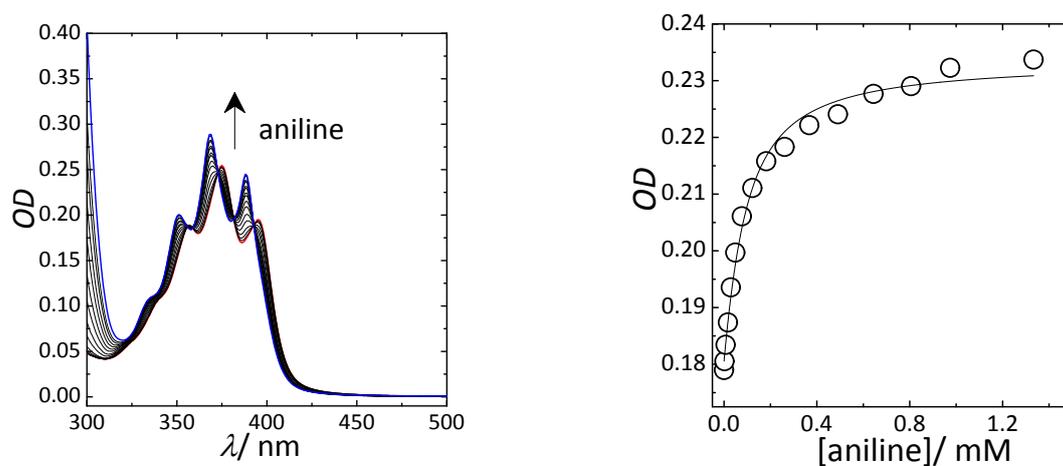


Figure S10. UV-Vis competitive titrations for the complexation of aniline with the CB8•AnPy reporter pair (35:35 μM) at pH 2.

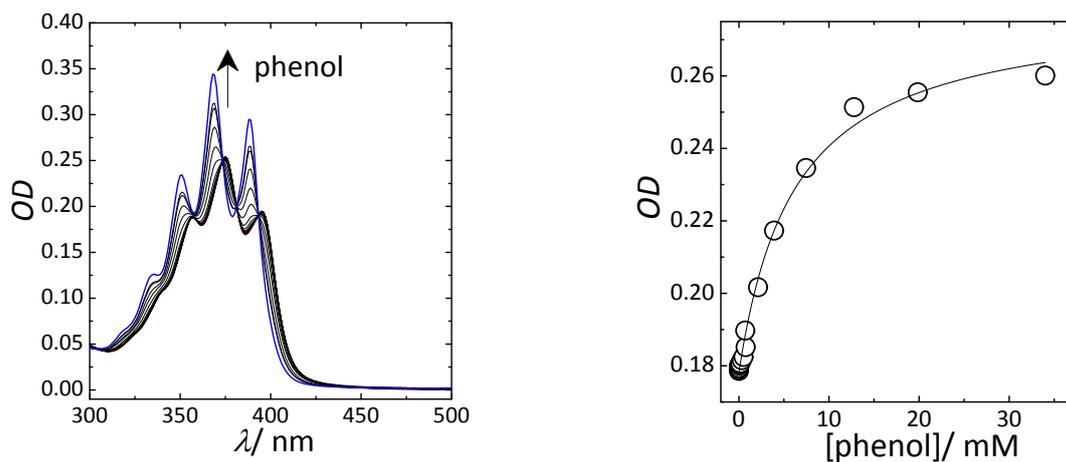


Figure S11. UV-Vis competitive titrations for the complexation of phenol with the CB8•AnPy reporter pair (35:35 μM) at pH 7.

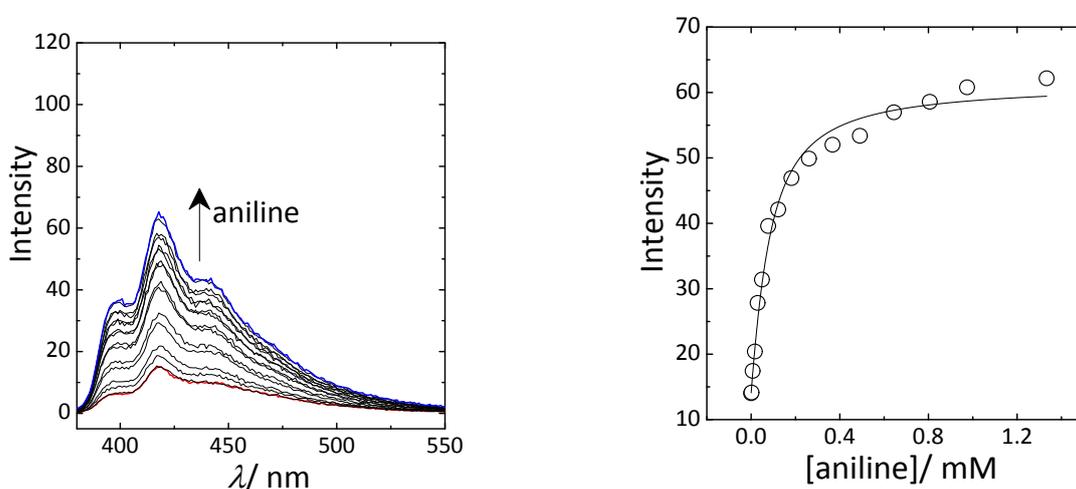


Figure S12. Fluorescence competitive titrations for the complexation of aniline with the reporter pair CB8•AnPy (35:35 μM) at pH 2.

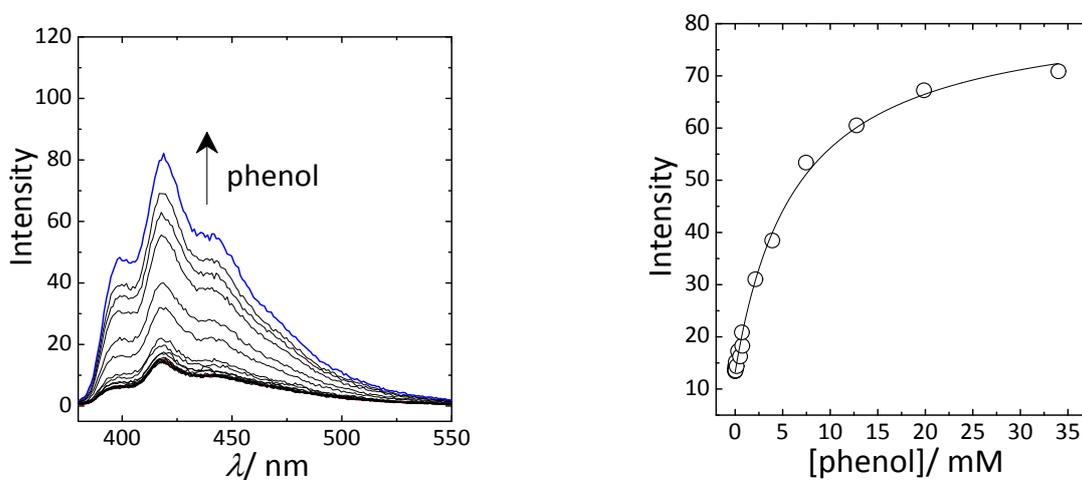


Figure S13. Fluorescence competitive titrations for the complexation of phenol with the reporter pair CB8•AnPy (35:35 μM) at pH 7.

6. Photo-oxidation Reaction of AnPy

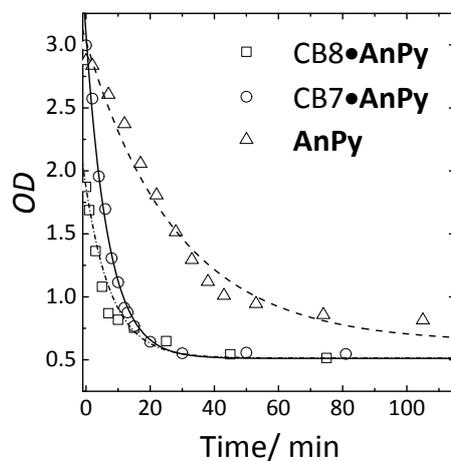


Figure S14. Monitoring of the photo-reaction of free (0.5 mM) and complexed **AnPy** (0.5 mM **AnPy** and 0.5 mM host) as a function of time.

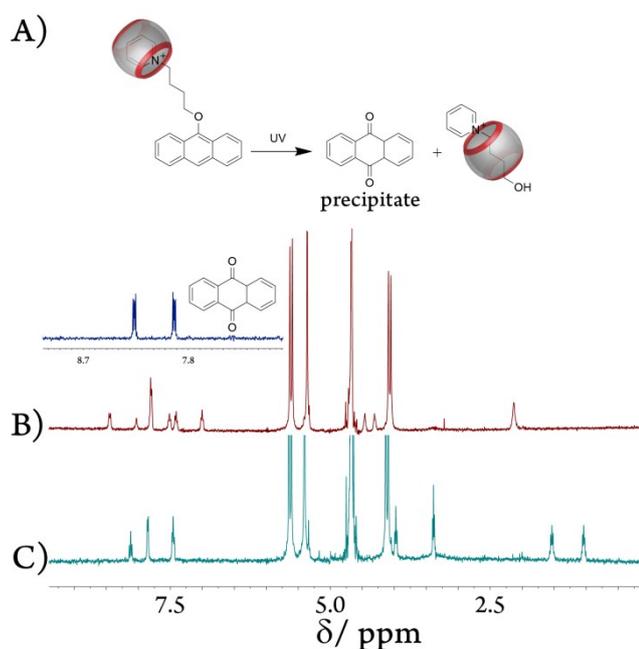


Figure 15. A) Photo-oxidation of **AnPy** upon UV-irradiation in aqueous solution. ^1H NMR spectra of CB7•**AnPy** (1 mM) in D_2O before (B) and after (C) UV-irradiation for 3 h. The ^1H NMR spectrum of the extracted anthraquinone in acetone- d_6 show in blue.

7. References

- [1] Y. X. Wang, Y. M. Zhang, Y. Liu, *J. Am. Chem. Soc.* 2015, **137**, 4543.
- [2] J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* 2000, **122**, 540.
- [3] C. Márquez, F. Huang, W. M. Nau, *IEEE Trans. Nanobiosci.* 2004, **3**, 39.