Supplementary Information

A Green to Blue Fluorescence Switch of Protonated 2-Aminoanthracene Upon Inclusion in Cucurbit[7]uril

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1. General Experimental

The 2-aminoanthracene (2-AA, Aldrich) was recrystallized from ethanol prior to use. The cucurbit[7]uril (CB[7]) was prepared by a literature method and vacuum dried before use.[1] The {2-AAH•CB[7]}$^+$ inclusion complex was prepared from mixing a 1:1.5 ratio of 2-AA and CB[7] together in acidic aqueous solution with the pH was adjusted to 1.5 with hydrochloric acid.

^{1}H NMR spectrum of 2-AAH$^+$ (400 MHz, D$_2$O, pH = 1.5): δ 8.57 (s, 1H), 8.54 (s, 1H), 8.16 (d, J = 9.3 Hz, 1H), 8.05 (m, 2H), 7.51 (m, 2H), 7.35 (d, J = 9.3 Hz, 1H) ppm.

^{1}H NMR spectrum of {2-AAH•CB[7]}$^+$ (Figure S1) (400 MHz, D$_2$O, pH = 1.5): δ 8.21 (broad, 1H), 8.11 (broad, 1H), 7.65 (s, 1H), 7.48 (s, 1H), 7.34 (m, 2H), 7.18 (d, J = 8.7 Hz, 1H), 6.83 (d, J = 8.7 Hz, 1H), 5.60 (d, J = 15 Hz, 7H, CB[7]), 5.44 (d, J = 15 Hz, 7H, CB[7]), 5.27 (s, 14H, CB[7]), 4.05 (d, J = 15 Hz, 7H, CB[7]), 3.93 (d, J = 15 Hz, 7H, CB[7]) ppm. **ESI-MS:** [M+2H]$^{2+}$ m/z = 679.3, calculated 678.7
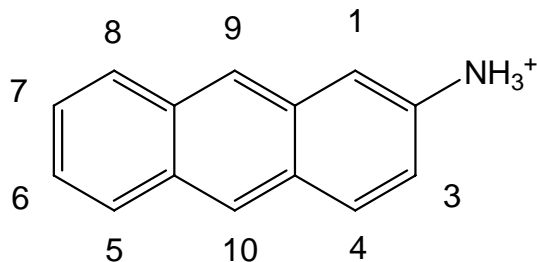
Scheme S1. Proton numbering scheme for **2-AAH$^+$**.

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[1] A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094.
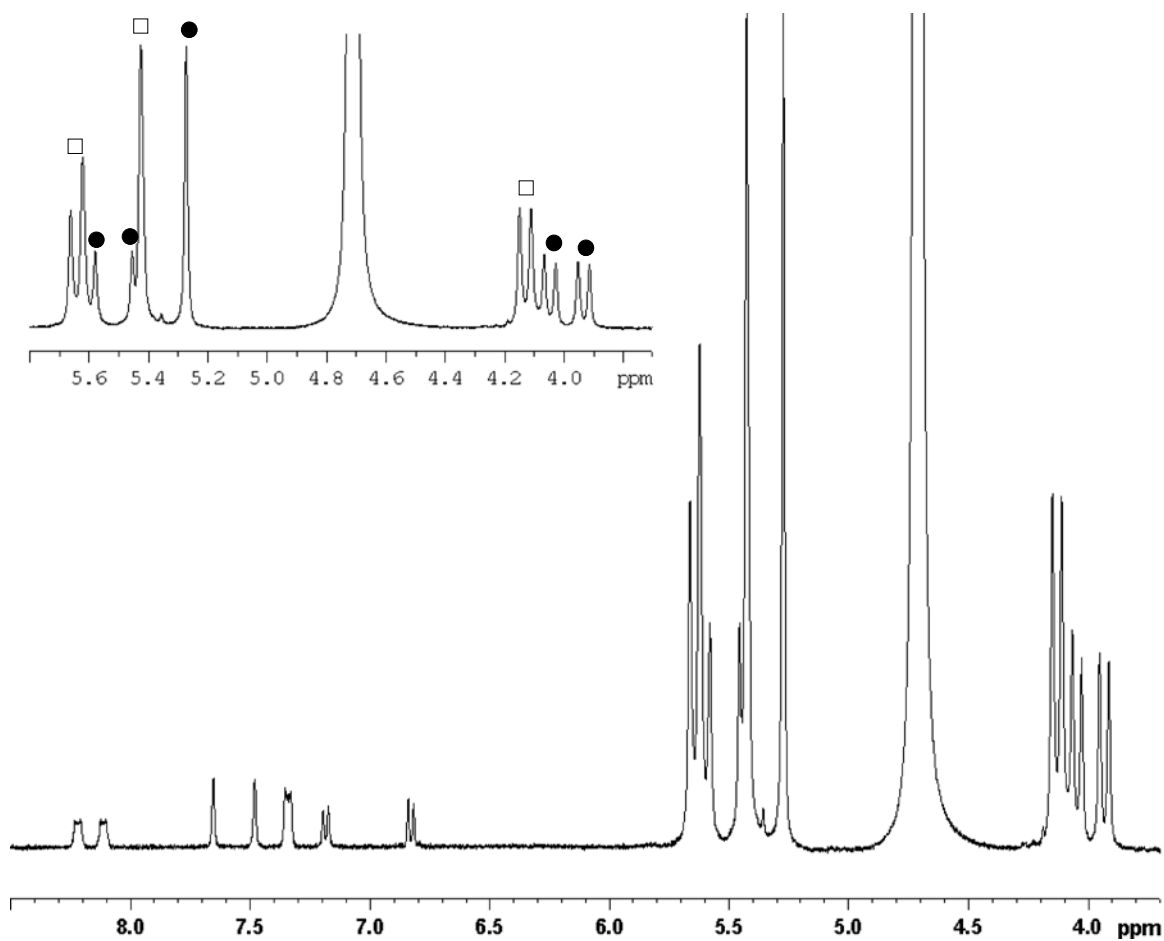
Figure S1. The ^{1}H NMR spectrum of {2-AAH•CB[7]}$^+$ in D$_2$O in the presence of an excess of CB[7]. In the top section the resonances for the CB[7] host protons are shown, with the free CB[7] proton resonances indicated by (□) and the proton resonances of the host in {2-AAH•CB[7]}$^+$ indicated by (●).
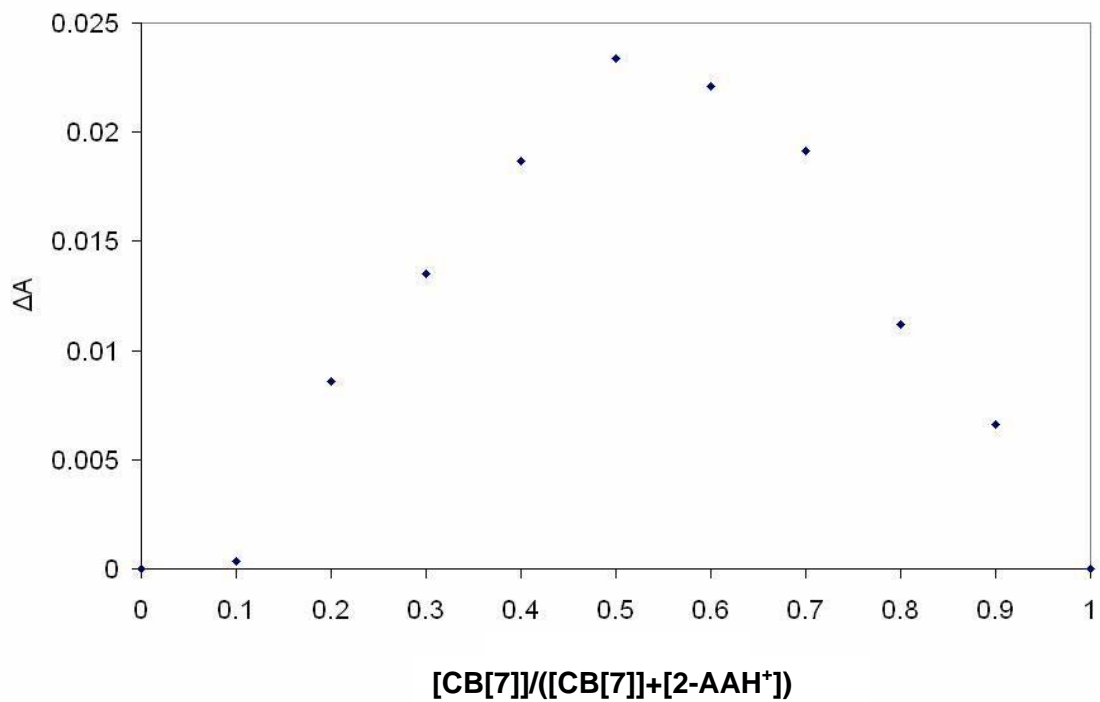
Figure S2. A continuous variation Job's plot of the change in the UV-visible absorption spectrum showing the 1:1 stoichiometry of the complexation of CB[7] with 2-AAH$^+$. The absorbance difference at 358 nm was used for the plot, with [2-AAH$^+$] + [CB[7]] = 50 μM.
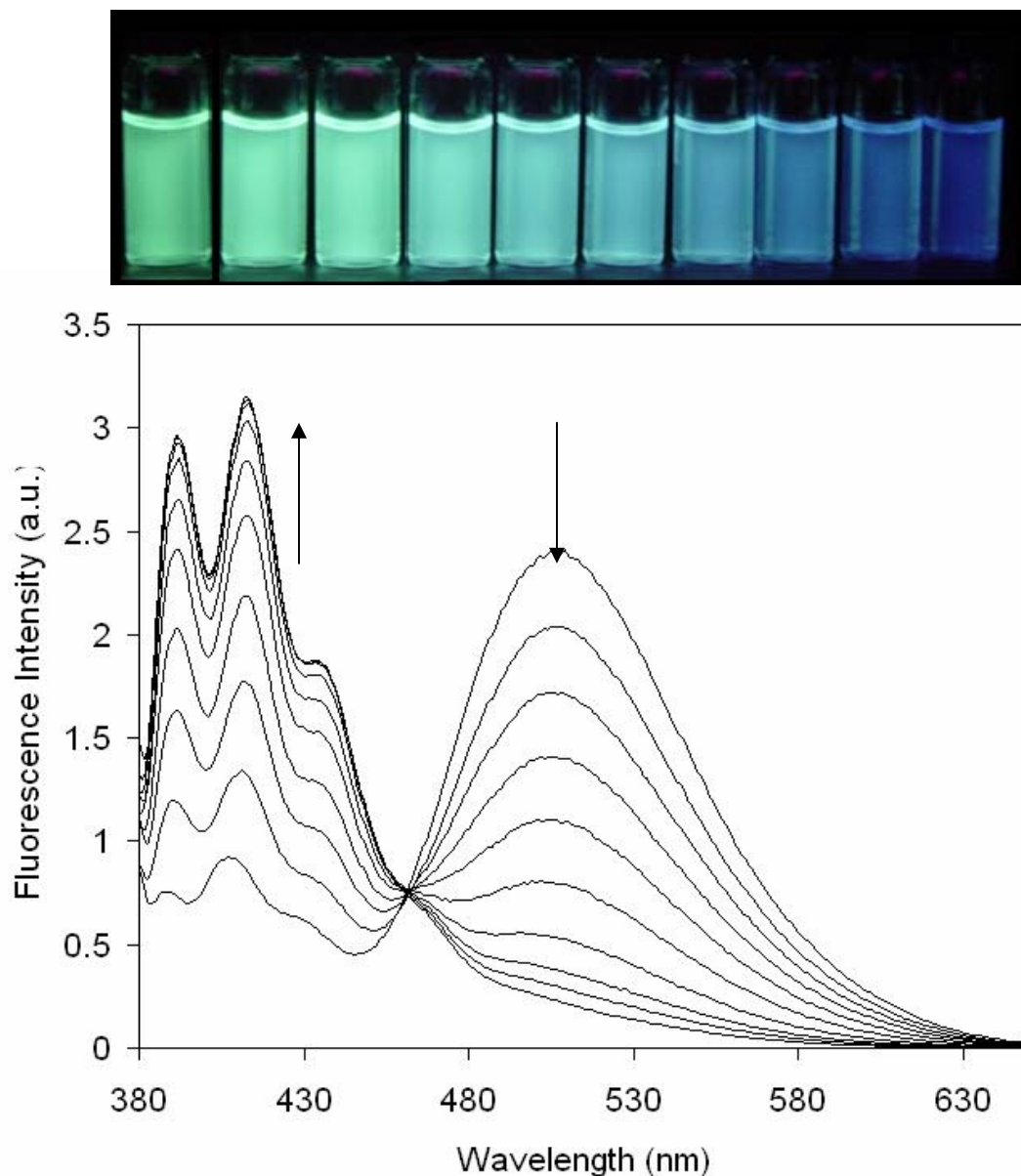
Figure S2: Bottom: Fluorescence spectra (excitation at 374 nm) of 2-AAH$^+$ without CB[7] and with various amounts of CB[7] (0.2:1, 0.4:1, 0.6:1, 0.8:1, 1:1, 1.2:1, 1.4:1, 1.6:1 and 2:1 ratio of CB[7]:2-AAH$^+$). The fluorescence at 512 nm is suppressed with increasing CB[7] while the fluorescence at about 406 nm is enhanced by complexation by CB[7]. **Top:** Digital images of an aqueous solution of 2-AAH$^+$ (50 μM) with different ratios of CB[7]:2-AAH$^+$ (from left to right: 0:1, 0.2:1, 0.3:1, 0.4:1, 0.5:1, 0.6:1, 0.7:1, 0.8:1, 0.9:1, 1.0:1, and 1.2:1 ratios) under a UV lamp (365 nm wavelength).

Calculations of pKa (ground state) and pKa* (excited singlet state):

1) The pKa of {2-AAH$^+$•CB[7]}$^+$ in the ground state was measured by adding half equivalent hydrochloric acid into 25uM {2-AA•CB[7]}. Assuming {2-AA•CB[7]} is a strong base, half of the {2-AA•CB[7]} becomes protonated and becomes {2-AAH•CB[7]}$^+$ after adding half an equivalent of acid, while the other half remains unprotonated {2-AA•CB[7]}, according to the following equation:

$$pKa = pH + \log([\{2\text{-}AAH\text{•}CB[7]\}^+]/[\{2\text{-}AA\text{•}CB[7]\}])$$

where [{2-AAH•CB[7]}$^+$] = [2-AA•CB[7]] and pKa = pH. The pKa was determined to be 7.1 ± 0.2.

2) The pK_a* of {2-AAH•CB[7]}$^+$ (excited state) was initially measured and calculated from:

a) **Förster's cycle**:

$$pK_a* = pK_a - 0.625*\Delta v/T$$

assuming that ($\Delta S* - \Delta S^0$) is equal to zero.[22] The value of Δv was measured to be 2431 cm^{-1}, and therefore, the $(pK_a)_{Fc}*$ was calculated to be 2.0. This value is not accurate as ($\Delta S* - \Delta S^0$) is not zero. It is, however, difficult to correct for ($\Delta S* - \Delta S^0$) because of the complication of host-guest interactions involved in this particular complex. Fortunately, the value calculated from the Förster cycle method can be corrected for. It has been

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[2] T. Förster, *Z. Elecktrochem.*, 1950, **54**, 42.

proposed by Shizuka[3] that for aromatic amines the actual pKa^* can be estimated approximately from the values for (pKa^*)$_{FC}$ and the Stokes' shift ΔE_{St}:

$$pKa^* = (pKa^*)_{FC} + 8.72\Delta E_{St} - 2.64$$

where (pKa^*)$_{FC}$ is the pKa^* value calculated from Förster's cycle. The Stokes' shift is the difference in energy (eV) between the 342 nm excitation wavelength and the 412 nm emission maximum. ΔE_{St} is calculated from this shift to be 0.61 eV. The value of pKa^* = 2.0 + (8.72)(0.61) − 2.64 = 4.68.

b) **Fluorescence titration**:

A fluorescence titration was employed to estimate the pK_a^* value (Figure S1), from which the pKa^* was estimated to be 5.2 ± 0.2, which is fairy close to the value calculated from corrected Forster's cycle. Based on all three methods above, the pKa^* is estimated to be 5.0 ± 0.5, consistent with the observation of green emission from a solution of 2-aminoanthracene containing CB[7] above pH 5 and blue emission below pH 5.

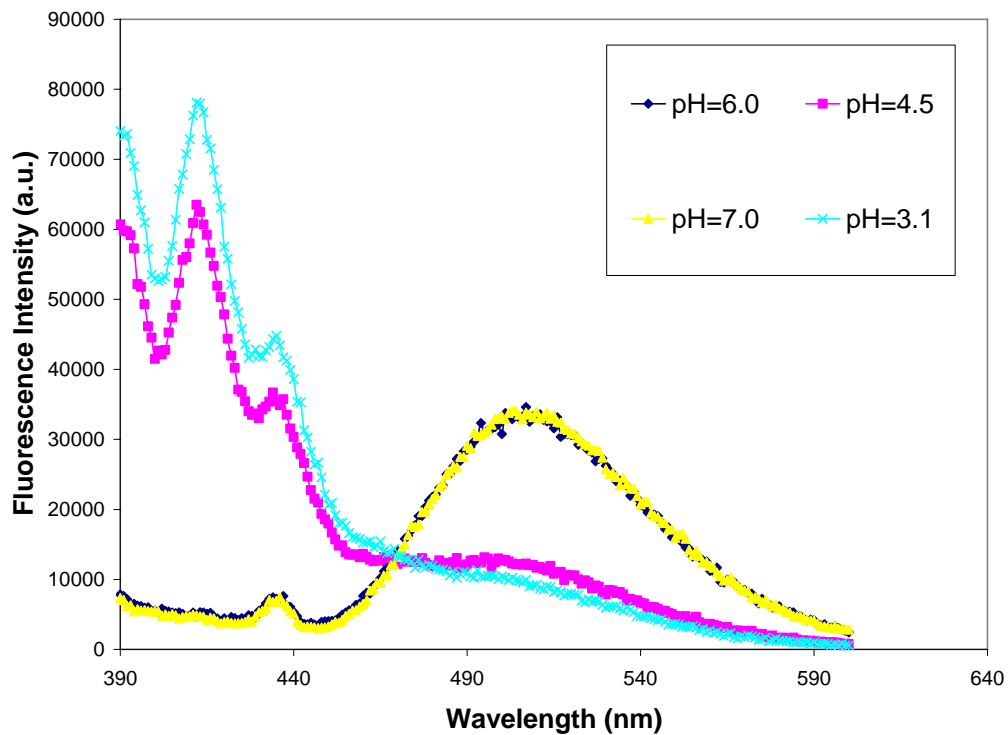[3] K. Tsutsumi, S. Sekiguchi and H. Shizuka, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1087

Figure S4 The dependence of the fluorescence spectrum of 1 μM {2-AAH@CB7}$^{+}$ on pH (excitation wavelength 370 nm).

Energy-minimized structures of 2-AAH$^+$ and {2-AAH•CB[7]}$^{2+}$

The structures of 2-AAH$^+$ and {2-AAH•CB[7]}$^{2+}$ were calculated using the Gaussian 03 suite of programs,[4] on the computing facilities of the High Performance Virtual Computing Laboratory (HPVCL) at Queen's University. The structures were initially constructed and minimized using ChemDraw and Chem 3D Pro (ChemOffice 7.0, CambridgeSoft) and the parameters were imported into Gaussian 03. The structures were calculated using a HF/3-21G** basis set.

[4] *Gaussian 03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford, CT, 2004.