A simple yet highly selective colorimetric sensor for cyanide anion in an aqueous environment

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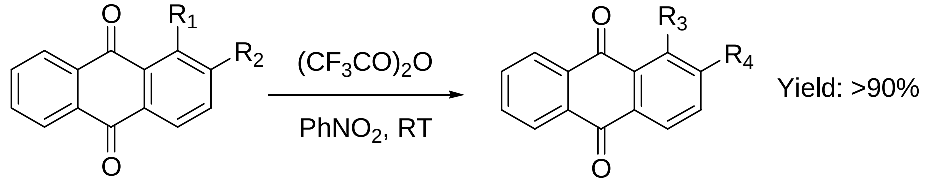
1 General methods

All chemicals and solvents obtained from commercial sources were analytical pure and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-P300 Spectrometer at 300 and 75 MHz respectively. Chemical shifts δ were reported in ppm relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. Mass spectra were recorded on a Finnigan LCQ-Advantage spectrometer. Elemental analyses were obtained using a Perkin-Elmer 2400C elemental analyzer. UV-vis spectra were taken on a Hitachi-3010 spectrophotometer.

The crystal data were measured on a BRUKER SMART 1000 CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) by ω scan mode at 113(2) K. All data were corrected by semi-empirical method using SADABS program. The program SAINT[1] was used for integration of the diffraction profiles. The structure was solved by the direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL.[2] The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. The hydrogen atoms of **2**·DMSO were placed in the geometrically calculated positions. All hydrogen atoms were included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded.

2 Synthesis of compound 1-TFAQ and 2-TFAQ



3 R_1=NH_2, R_2=H

4 R_1=H, R_2=NH_2

1 R_3=CF_3COONH_2, R_4=H

2 R_3=H, R_4=CF_3COONH_2

Scheme S1 Synthetic procedure of compounds **1** and **2**.

The two compounds were synthesized according to the literature method.[3] 1-aminoanthraquinone **3**/2-aminoanthraquinone **4** (2 g) was dissolved in nitrobenzene (25 mL). Trifluoroacetic anhydride (2.53 ml) was added to the solution, and the mixture was stirred under nitrogen for approximately 1 h. Nitrobenzene was removed by vacuum filtration. The yellow solid was washed with methanol to remove unreacted starting material, then purified via column chromatography with 1:5 ethyl acetate/petroleum ether on silica gel. Yield: >90%.

Compound **1** ^{1}H NMR (300 MHz, CD_3CN): δ 7.92-7.99 (m, 3H), 8.17-8.20 (d, 7.7 Hz, 1H), 8.26-8.29 (m, 1H), 8.32-8.35 (m, 1H), 8.95-8.98 (d, 8.3 Hz, 2H), 13.42 (s, 1H). ^{13}C NMR (CD_3CN): δ 113.73, 118.87, 124.40, 126.06, 127.23, 127.64, 132.70, 133.49, 134.19, 134.56, 134.96, 136.08, 139.28, 155.85, 181.90, 187.59. ESI-MS: m/z 318.39 $[M-H^+]^-$. Anal. calcd for $C_{16}H_8F_3NO_3$: C 60.20, H 2.53, N 4.39. Found: C 60.09, H 2.86, N 4.54..

Compound **2** ^{1}H NMR (300 MHz, CD_3CN): δ 7.89-7.92 (m,2H), 8.10-8.13 (m, 1H), 8.27-8.34 (m, 3H), 8.56 (s, 1H), 9.67 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 117.97, 125.69, 126.73, 126.79, 128.42, 129.85, 133.07, 134.09, 134.42, 134.66, 141.80, 154.79, 181.46, 182.09. ESI-MS: m/z 318.15 $[M-H^+]^-$. Anal. calcd for $C_{16}H_8F_3NO_3$: C 60.20, H 2.53, N 4.39. Found: C 60.19, H 2.77, N 4.41.

3 Crystal data and packing diagram of **2**·DMSO

Table S1 X-ray crystallographic data for compound **2**·DMSO.

	2·DMSO
Empirical formula	$C_{18}H_{14}F_3NO_4S$
Formula weight	397.36
Crystal system	Triclinic
Space group	P-1
a (Å)	8.5833(17)
b (Å)	10.109(2)
c (Å)	10.778(2)
α (°)	106.89(3)
β (°)	92.62(3)
γ (°)	108.79(3)
V (A^3)	837.1(3)
Z	2
D_{calcd} (g/cm^3)	1.576
μ(mm^{-1})	0.251
Total reflections	5992
Unique reflections	3883
R(int)	0.0239
R_1/wR_2 [$I > 2\sigma(I)$]	0.0359/0.1042
R_1/wR_2 (all data)	0.0450/0.1081
GoF on F^2	1.059

Table S2 Hydrogen bond parameters in crystal structure of **2**·DMSO.

D-H…A	D…A(Å)	H…A (Å)	∠D-H…A (deg)
N1-H1A…F1	2.801	2.483	103
N1-H1A…O4^{i}	2.782	1.937	167
C1-H1…O3	2.885	2.283	122
C8-H8…O3^{ii}	3.422	2.521	163
C17-H17B…O2^{iii}	3.287	2.446	146
C18-H18A…O1^{iv}	3.347	2.542	141

Symmetry code: i, x, 1+y, z; ii, -1+x, y, -1+z; iii, 1-x, 2-y, -z; iv, 1-x, 1-y, -z.

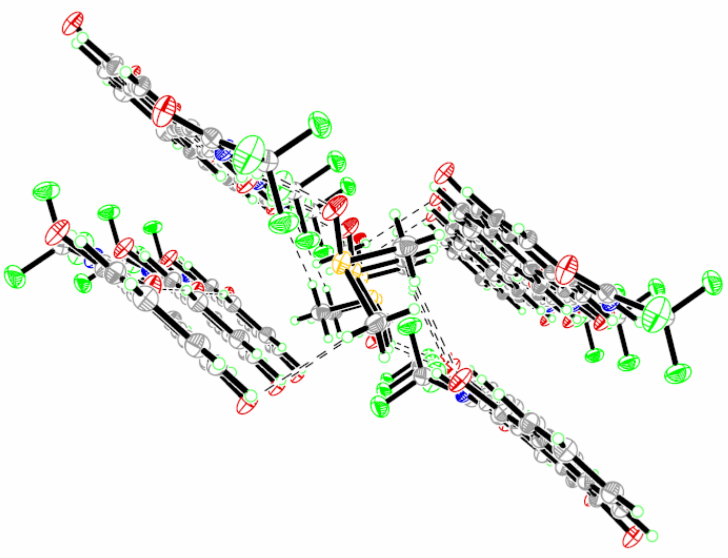


Figure S1 DMSO molecules linked supramolecular structures of **2**·DMSO.

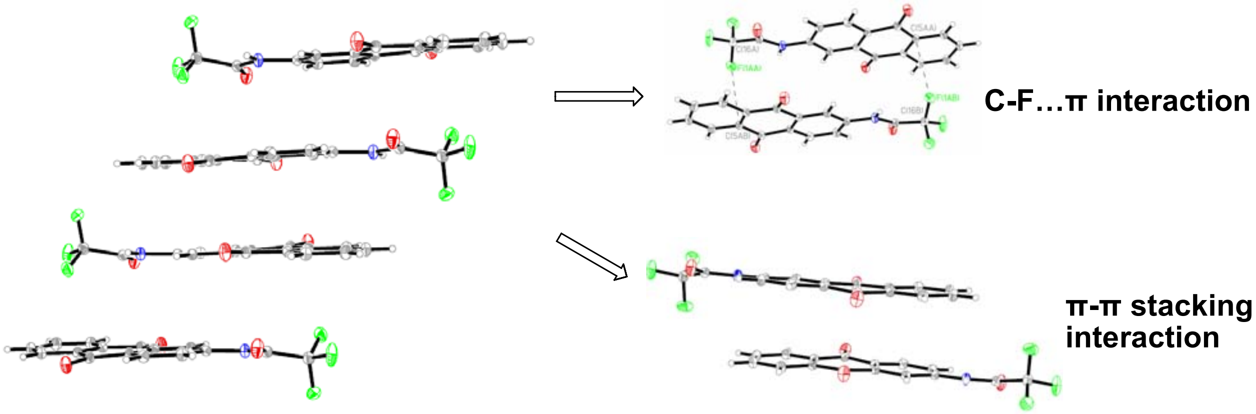


Figure S2 Packing diagram of **2** showing C–F**…**π interaction (distance: 3.092 Å) and π-π stacking interaction (distance: 3.374 Å).

4 Determination of the detection limit[4]

The detection limit DL of 2-(trifluoroacetylamino)anthraquinone **2** was determined from the following equation:

DL = K*Sb1/S

Where K = 3; Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

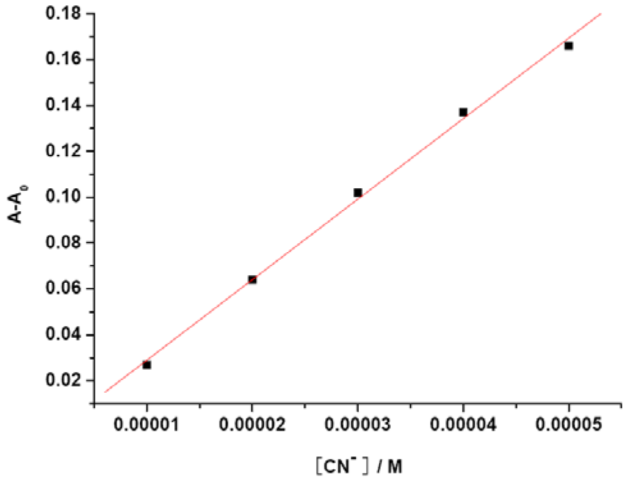
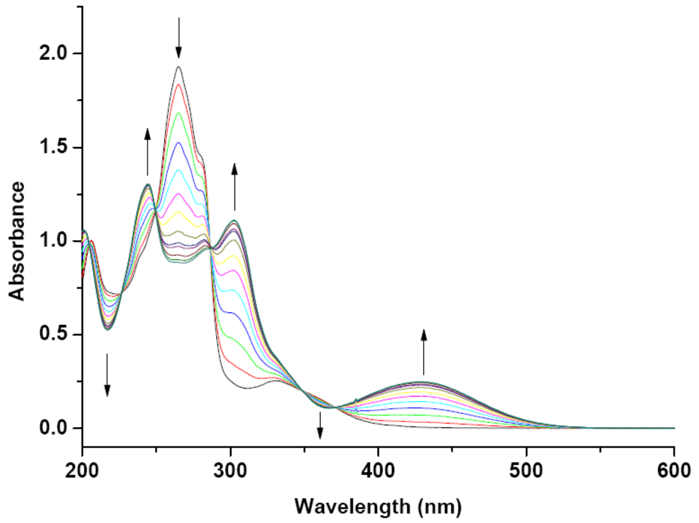


Figure S3 A plot of ($A-A_0$) vs CN^- concentrations at 429 nm.

Y = A + B * X

Parameter	Value	Error	
A	-0.0061	0.00336	
B	3510	101.15994	
R	SD	N	P
0.99876	0.0032	5	<0.0001

a)



b)

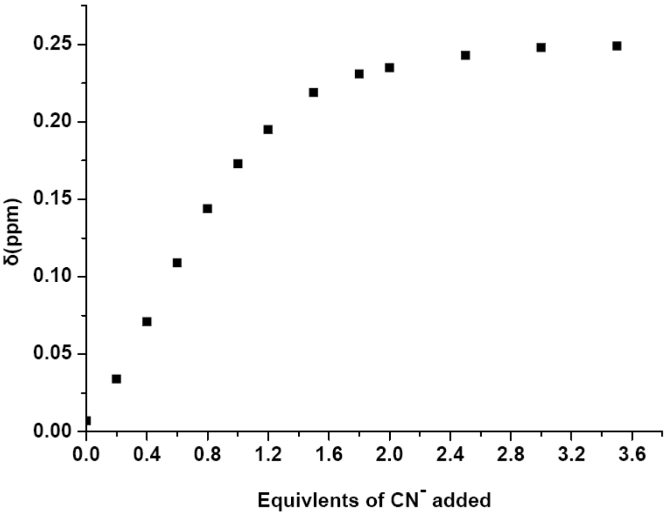


Figure S4 a) Changes observed in the absorption spectra of **2** (50 µM) upon addition of CN⁻ (0−1.75×10^{-4} M) in CH_3CN/H_2O (95:5, v/v) solution. b) Plot of the absorption value at 429 nm vs the equivalents of CN⁻.

References

1 *Bruker AXS*; SAINT Software Reference Manual: Madison, WI, 1998.

2 G. M. Sheldrick, *SHELXTL NT*: *Program for Solution and Refinement of Crystal Structures*, version 5.1; University of Göttingen: Göttingen, Germany, 1997.

3 S. J. Schmidtke, D. F. Underwood and D. A. Blank, *J. Phys. Chem. A*, 2005, **109**, 7033.

4 M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang and D. Zhu, *Org. Lett.*, 2008, **10**, 1481.