Electronic Supplementary Information (ESI)

Anion Identification using Silsesquioxane Cages

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Chemicals and Instruments

9-Bromoanthracene, PPh₃, triethylamine, tetrabutylammonium salts and Pd(OAc)$_2$ were purchased from TCI Chemicals and Sigma Aldrich, while octavinylsilsesquioxane (OVS) was prepared according to a previous literature report.¹ The list of chemicals suppliers are provided table S1. Deionized (DI) water was obtained from Ultra Clear SIEMENS with ASTM type 2. The commercial solvents of acetone, DCM, were further distilled. The AR grade of THF, Toluene, DMF and DMSO were used without purification. The silica gel (No. 60) used for column chromatography were purchased from Merck&Co., Inc. $^{19}$F NMR results were obtained using a Bruker-AV 400 high-resolution magnetic resonance spectrometer. FT-IR spectra were recorded using the attenuated total reflectance (ATR) technique on a Bruker model Alpha spectrometer. High-performance MALDI-TOF analysis was performed on a Bruker autoflexTM series instrument. UV-Vis spectroscopy was performed on a UV-Vis spectrophotometer (Shimadzu UV-2600), while all fluorescence spectra were recorded using a spectrofluorometer (Horiba FluoroMax4+, integration time 0.1 s, slit width 2 nm). These conditions were also employed for measurement of quantum yields, although such measurements required the use of a BaO coated spherical cube.

Table S1. List of chemicals

| Chemicals                        | Chemical formula | Suppliers                   |
|----------------------------------|------------------|-----------------------------|
| 9-Bromoanthracene                | C₁₄H₁₀Br         | Tokyo Chemical Industry     |
| tetrabutylammonium bromide (TBABr) | (C₁₆H₃₆N)Br     | Tokyo Chemical Industry     |
| tetrabutylammonium chloride (TBACl) | (C₁₆H₃₆N)Cl     | Tokyo Chemical Industry     |
| tetrabutylammonium cyanide (TBACN) | (C₁₆H₃₆N)CN     | Tokyo Chemical Industry     |
| tetrabutylammonium fluoride (TBAF) | (C₁₆H₃₆N)F      | Sigma Aldrich               |
| tetrabutylammonium nitrate (TBANO₃) | (C₁₆H₃₆N)NO₃   | Tokyo Chemical Industry     |
| tetrabutylammonium phosphate (TBAPO₄) | (C₁₆H₃₆N)₃PO₄ | Tokyo Chemical Industry     |
| tetramethylammonium hydroxide (TBAOH) | (C₄H₁₂N)OH     | Sigma Aldrich               |
| Triethylamine                    | C₆H₁₅N          | Tokyo Chemical Industry     |
| Triphenylphosphine               | P(C₆H₅)$_3$      | Tokyo Chemical Industry     |
| Palladium(II) acetate            | Pd(OAc)$_2$     | Tokyo Chemical Industry     |

Reference

1. Harrison, P. G., & Hall, C. (1997), Main Group Metal Chemistry, 20(8), 515–530.
Synthesis of anthracene-conjugated octameric silsesquioxane cages (AnSQ)

The AnSQ cage was prepared using a Heck coupling methodology. An oven-dried (100 °C) 100 ml 2-necked round bottom flask was charged with 632 mg of OVS (1 mmol), 90 mg of palladium (II) acetate (0.4 mmol) and 210 mg of triphenylphosphine (0.8 mmol) along with a stirring magnetic bar. After evacuation for 30 minutes, an argon flow was introduced, followed by a THF/Et3N (30/15 ml) solution. After bubbling argon through the solution for 30 minutes, a separately prepared solution of 3.217 g (12 mmol) of 9-bromoanthracene in 15 ml of dry THF was injected into the mixture. The reaction was stirred and heated at 80 °C for 48 hours. Work-up involved cooling to room temperature and removal of insoluble catalyst by filtration. The clear solution mixture was diluted with 200 ml of 0.5% HCl in MeOH to remove excess base, affording a precipitate which was collected and re-dissolved in the minimum volume of CH2Cl2. Flash column chromatography on silica gel using 100% CH2Cl2 as eluent afforded a residue that was purified by Soxhlet extraction, first with MeOH and then with hexane (one day per extraction). The bright yellow solid obtained 1.76 g (86 % yield) was stored under inert atmosphere in the refrigerator.

Quantum efficiency measurement

The quantum efficiencies were measured by comparing between solvents as a blank and sample according to this equation (original from Horiba with sphere cuvette correction):

\[
\phi_P = \frac{\Delta \text{Area under emission curve}}{\Delta \text{Area under absorption curve}}
\]

the default mode for quantum yield measurement was set at slitwidth 3 nm, integration time 1 sec and increment of emission 3 nm per step. After that parabolic spherical barium oxide was equipped to cover the quartz cell. This quantum efficiency measurement does not require reference, except for calibration using Rhodamine B. 100 equiv. of anions were added into 6 μM of AnSQ and wait 18 hours before measurement to reach the equilibrium (Fig S3, table 1).
Quantitative Analysis of Anion Detection

A polar solvent, DMSO, was selected for anion association studies due to high complex stability, fast formation kinetics and strong excimer emission in this medium. Binding, or association, constants \( (K_a) \) were calculated using the Benesi-Hildebrand equation as below.

(a) for fluorescence studies and (b) for absorption studies

\[
\frac{1}{I-I_0} = \frac{1}{I'-I_0} + \frac{1}{(I'-I_0)K_a[A^-]} \quad (a)
\]

\[
\frac{1}{A-A_0} = \frac{1}{A'-A_0} + \frac{1}{(A'-A_0)K_a[A^-]} \quad (b)
\]

In equations (a) and (b), \( I_0 \) and \( I \) refer to fluorescence intensities prior to, and post-anion addition. Likewise, \( A_0 \) and \( A \) refer to absorbance values prior to, and post-anion addition.

Limits of detection (LOD) and quantitation (LOQ) were obtained from titration results and calculated from the linear region using the following equations, with \( S_b \) referring to the standard deviation.

The standard deviation (\( S_b \)) can be calculated by the below equation, where \( S \) is the slope of the calibration curve.

\[
S_b = \frac{S_y/x}{\sqrt{\sum_i(x_i-x)^2}} \quad S_y/x = \sqrt{\frac{\sum_i(y_i-y)^2}{n-2}}
\]

In this work, the \( x \) value refers to the concentration of added anions, with \( y \) reflecting the fluorescence intensity and absorbance values.
Figure S1. MALDI-TOF spectrum of AnSQ [M+H]^+ from OVS : 9-bromoanthracene = 1 : 12 via heck coupling reaction.
**Figure S2a.** Solid state of 9-bromoanthracene, AnSQ and AnSQ after fluoride addition at solid state under visible light and UV lamp PL series handheld split-tube lamp, model UVGL-55 at $\lambda_{ex} = 365$ nm
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Figure S3ab. Quantum yield of AnSQ-Br⁻ in acetone
Figure S3ac. Quantum yield of AnSQ-Cl\textsuperscript{-} in acetone

Figure S3ad. Quantum yield of AnSQ-CN\textsuperscript{-} in acetone
**Figure S3ae.** Quantum yield of AnSQ-F⁻ in acetone

**Figure S3af.** Quantum yield of AnSQ-NO₃⁻ in acetone
Figure S3ag. Quantum yield of AnSQ-OH⁻ in acetone

Figure S3ah. Quantum yield of AnSQ-PO₄³⁻ in acetone
Figure S3ai. Quantum yield of AnSQ in DCM

Figure S3aj. Quantum yield of AnSQ-Br in DCM
Figure S3aj. Quantum yield of AnSQ-Cl$^-$ in DCM

Figure S3ak. Quantum yield of AnSQ-CN$^-$ in DCM
Figure S3al. Quantum yield of AnSQ-F in DCM

Figure S3am. Quantum yield of AnSQ-NO$_3$ in DCM
**Figure S3an.** Quantum yield of AnSQ-OH⁻ in DCM

**Figure S3ao.** Quantum yield of AnSQ-PO₄³⁻ in DCM
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**Figure S3as.** Quantum yield of AnSQ-CN⁻ in DMF
**Figure S3at.** Quantum yield of AnSQ-F\(^-\) in DMF

**Figure S3au.** Quantum yield of AnSQ-NO\(_3^-\) in DMF
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Figure S3aw. Quantum yield of AnSQ-PO₄³⁻ in DMF
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Figure S3bc. Quantum yield of AnSQ-NO\(_3^{-}\) in DMSO
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**Figure S3bu.** Quantum yield of AnSQ-OH\(^-\) in THF+H\(_2\)O

**Figure S3bv.** Quantum yield of AnSQ-PO\(_4^{3-}\) in THF+H\(_2\)O
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**Figure S11b.** FTIR of solid state AnSQ+TBAF. The peaks at 1072 cm\(^{-1}\) is assigned as Si-O-Si stretching, and the peaks at 734 cm\(^{-1}\) is assigned as Si-O-Si bending.
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**Figure S11d.** FTIR of solid state AnSQ+TBAOH. The peaks at 1094 cm\(^{-1}\) is assigned as Si-O-Si stretching, and the peaks at 731 cm\(^{-1}\) is assigned as Si-O-Si bending, the peak at 952 cm\(^{-1}\) is assigned as O-H bending.
**Figure S11e.** FTIR of solid state AnSQ+TBAPO$_4$. The peaks at 1098 cm$^{-1}$ is assigned as Si-O-Si stretching, and the peaks at 732 cm$^{-1}$ is assigned as Si-O-Si bending, the characteristic peak of phosphate is dominated by Si-O-Si stretching.

**Figure S11f.** FTIR of solid state AnSQ+TBABr. The peaks at 1090 cm$^{-1}$ is assigned as Si-O-Si stretching, and the peaks at 732 cm$^{-1}$ is assigned as Si-O-Si bending.
Figure S11g. FTIR of solid state AnSQ+TBACl. The peaks at 1092 cm\(^{-1}\) is assigned as Si-O-Si stretching, and the peaks at 734 cm\(^{-1}\) is assigned as Si-O-Si bending.

Figure S11h. FTIR of solid state AnSQ+TBANO\(_3\). The peaks at 1094 cm\(^{-1}\) is assigned as Si-O-Si stretching, and the peaks at 734 cm\(^{-1}\) is assigned as Si-O-Si bending. The characteristic of nitrate peak is assigned at 1334 cm\(^{-1}\).