Supporting Information

Supramolecular Association of Dopamine with Immobilized Fluorescent Probes

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Preparation of the Fluorescent Particles and Their Precursors

*Hexafluorophosphate salt of **2**:* A solution of 2,7-diazapyrene[1] (245 mg, 1 mmol) in PhMe (20 mL) was heated under reflux and then benzyl bromide (500 μL, 4 mmol) was added dropwise over 10 min. The resulting mixture was maintained under reflux for 1 h. After cooling down to ambient temperature, it was filtered and the solid residue was washed with Et_2O (40 mL) and dissolved in H_2O/Me_2CO (1:1, 40 mL). After the addition of NH_4PF_6 (3 g), the aqueous solution was stirred for 30 min at ambient temperature and then it was concentrated to a volume of 15 mL under reduced pressure. The resulting precipitate was filtered and washed with H_2O (20 mL) to give the hexafluorophosphate salt of **3** (240 mg, 83%) as a yellowish solid. mp = 216–218°C (decomposition); FABMS: *m/z* = 295 $[M - PF_6]^+$; ^{1}H-NMR (300 MHz, CD_3CN): δ = 9.84 (2H, s), 9.69 (2H, s), 9.68 (2H, d, J_{AB} = 9.2 Hz), 8.50 (2H, d, J_{AB} = 9.2 Hz), 7.64–7.59 (2H, m), 7.53–7.48 (3H, m), 6.17 (2H, s); ^{13}C-NMR (100 MHz, CD_3CN): δ = 149.34, 139.36, 134.58, 132.35, 131.11, 130.68, 130.46, 130.37, 129.97, 127.09, 126.96, 125.25, 67.02.

4-Chloromethylphenyl-coated particles: **1** (4.5 mL) was added to a suspension of silica particles (500 mg, surface density = 200 $m^2 g^{-1}$) in dry PhMe (25 mL). The mixture was stirred for 12 h at 50°C under N_2. After filtration, the solid residue was washed with PhMe for 12 h in a continuous solid/liquid extraction apparatus.

2,7-Diazapyrenium-coated particles: 4-Chloromethylphenyl-coated particles (250 mg) were suspended in a solution of the hexafluorophosphate salt of **2** (22 mg) in dry MeCN (5 mL). The mixture was stirred for 1 h at 50°C. After filtration, the solid residue was washed with MeCN for 12 h in a continuous solid/liquid extraction apparatus. Combustion analysis revealed a C content of 0.13 mg per mg of particles.

Fluorescence Measurements

*Bis(hexafluorophosphate) salt of **3**:*[2] The emission and excitation spectra were recorded in MeCN at 25°C using a Varian Cary Eclipse. The concentration of the analyte was 1.2×10^{-5} M and the emission and excitation wavelengths were 432 and 342 nm, respectively.

2,7-Diazapyrenium-coated particles: The fluorescent particles (1 mg) were suspended in MeCN (2 mL) and the emission and excitation spectra were recorded under constant stirring at 25°C using a Varian Cary Eclipse. The emission and excitation wavelengths were 432 and 342 nm, respectively.

Titrations: The fluorescent particles (5 mg) were suspended in sodium phosphate buffer (15 mL, *p*H = 7). Increasing amounts of a solution (1 M) of dopamine, catechol or propylamine in the same buffer were added to the suspension. Using this procedure, the concentration of the analyte was raised from 10^{-4} to 10^{-1} M in ten consecutive steps. At each step, the emission spectrum was recorded under constant stirring at 32°C using a Varian Cary Eclipse. The excitation wavelength was 342 nm. The titrations of the bis(hexafluorophosphate) salt of **3** (3.0×10^{-5} M) and of the fluorescent particles (0.3 mg mL^{-1}) with catechol were performed in MeCN under otherwise identical conditions.

Binding model: Each 2,7-diazapyrenium dication (the receptor) has two electron deficient faces. As a result, the concomitant formation of 1:1 and 1:2 complexes is possible in the presence of an excess of an electron rich analyte (the substrate). Therefore, the analysis of the influence of the substrate concentration on the emission intensity requires a multiple equilibria binding model.[3]

The electron rich substrates employed do not emit in the wavelength range probed. The 2,7-diazapyrenium dications, in their free and complexed forms, are responsible for the emission at 432 nm. Thus, the intensity (I) measured at this wavelength is equal to the sum of the emission intensities of the free receptor (I_R), the 1:1 complex (I_{C1}) and the 1:2 complex (I_{C2}) (eq. 1). Proportionality constants (k_R, k_{C1} and k_{C2}) correlate I_R, I_{C1} and I_{C2} to the concentrations of the receptor ([R]), the 1:1 complex ([C1]) and the 1:2 complex ([C2]) (eq. 2–4).[4] The combination of eq. 1–4 correlates I with the concentrations of all three species (eq. 5).

$$I = I_R + I_{C1} + I_{C2} \quad (1)$$

$$I_R = k_R [R] \quad (2)$$

$$I_{C1} = k_{C1} [C1] \quad (3)$$

$$I_{C2} = k_{C2} [C2] \quad (4)$$

$$I = k_R [R] + k_{C1} [C1] + k_{C2} [C2] \quad (5)$$

The total concentration of the 2,7-diazapyrenium dication (c_R) is the sum of [R], [C1] and [C2] (eq. 6). Before the addition of the substrate, [C1] and [C2] are equal to 0. As a result, c_R is equal to [R] and eq. 5 simplifies to eq. 7, where I_0 is the initial emission intensity. The combination of eq. 5 and 7 affords eq. 8.

$$c_R = [R] + [C1] + [C2] \quad (6)$$

$$I_0 = k_R c_R \quad (7)$$

$$\frac{I}{I_0} = \frac{[R]}{c_R} + \frac{k_{C1}}{k_R}\frac{[C1]}{c_R} + \frac{k_{C2}}{k_R}\frac{[C2]}{c_R} \quad (8)$$

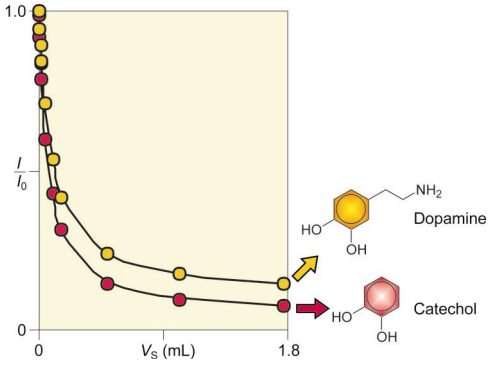

Figure S1. Plots of the ratio between I and I_0 against V_s for the titrations of the fluorescent particles with catechol or dopamine.

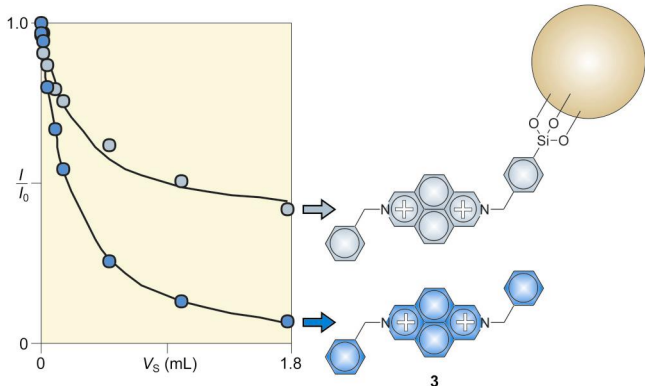

Figure S2. Plots of the ratio between I and I_0 against V_s for the titrations of **3** or the fluorescent particles with catechol.

The association constants for the 1:1 (K_1) and 1:2 (K_2) complexes are related to [R], [C1], [C2] and the concentration of the substrate ([S]) according to eq. 9 and 10. The combination of eq. 6 and 8–10 gives eq. 11. Since the substrate is in large excess relative to the receptor, [S] can be considered to be equal to the total concentration of the substrate (c_S) (eq. 12).

$$K_1 = \frac{[C1]}{[R][S]} \quad (9)$$

$$K_2 = \frac{[C2]}{[C1][S]} \quad (10)$$

$$\frac{I}{I_0} = \frac{1 + \frac{k_{C1}}{k_R} K_1 [S] + \frac{k_{C2}}{k_R} K_1 K_2 [S]^2}{1 + K_1 [S] + K_1 K_2 [S]^2} \quad (11)$$

$$c_S = [S] \quad (12)$$

The titrations are performed adding increasing amounts of a solution of the substrate to either a suspension of the fluorescent particles or a solution of **3**. As a result, c_S is related to the volume (V_S) and molarity (M_S) of the substrate solution added and to the initial volume (V_0) of the suspension or solution containing the receptor (eq. 13). Combining eq. 11–13, the ratio between I and I_0 becomes a function of V_S (eq. 14).

$$c_S = \frac{V_S M_S}{V_0 + V_S} \quad (13)$$

$$\frac{I}{I_0} = \frac{1 + \frac{k_{C1}}{k_R} K_1 \frac{V_S M_S}{V_0 + V_S} + \frac{k_{C2}}{k_R} K_1 K_2 \left(\frac{V_S M_S}{V_0 + V_S}\right)^2}{1 + K_1 \frac{V_S M_S}{V_0 + V_S} + K_1 K_2 \left(\frac{V_S M_S}{V_0 + V_S}\right)^2} \quad (14)$$

The intensities I and I_0 are measured experimentally. The volumes V_0, V_S and the molarity M_S are known. The analysis of a plot of the ratio between I and I_0 against V_S with a curve fitting program[5] affords the association constants K_1 and K_2. Figures S1 and S2 illustrate the curve-fitting for the four complexation processes analyzed. In all instances, the coefficient of determination for the fit was greater than 0.99.

(1) 2,7-Diazapyrene was synthesized in three steps starting from 1,4,5,8-naphthalenetetracarboxylic dianhydride and following a literature procedure. Hünig, S.; Gross, J.; Lier, E. F.; Quast, H. *Liebigs Ann. Chem.* **1973**, 339–358.

(2) The bis(hexafluorophosphate) salt of **3** was prepared in one step starting from 2,7-diazapyrene and following a literature procedure. Ashton, P. R.; Boyd, S. E.; Brindle, A.; Langford, S. J.; Menzer, S.; Pérez-García, L.; Preece, J. A.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *New J. Chem.* **1999**, *23*, 587–602.

(3) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.

(4) Note that a linear correlation between the emission intensity and the fluorophore concentration applies only to concentration ranges which ensure a very low absorbance at the excitation wavelength (Sharma, A.; Schulman, S. G. Introduction to Fluorescence Spectroscopy; Wiley: New York, 1999). The experimental conditions of the reported binding studies were chosen to satisfy this condition.

(5) PSI-Plot 6.0a, Poly Software International, Inc., 1999.