Supporting Information

Pyridinium/urea based anion receptor: methine formation in the presence of basic anions

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Synthesis of 1

To a solution of alkyne, N-(4-trifluoromethylphenyl)-N’-(4’-ethynylphenyl)urea, (0.35 g, 1.30 mmol) and 2-(azidomethyl)pyridine\[1-2\] (0.21 g, 1.52 mmol) in 20 ml methanol/t-butanol 1:1 (v:v) mixture was added a solution of Cu(OAc)$_2$·H$_2$O (13 mg, 0.065 mmol) in 1 ml of water. The reaction mixture was stirred at room temperature. After 18 h stirring, a white precipitate was filtered out (yield 80%, 0.45 g). ESI-MS (CH$_3$CN): $m/z$ (–) 473 [M + Cl]–; UV–vis. (CH$_3$CN): $\lambda$$_{max}$ = 282 nm, $\varepsilon$_{282} = 52 × 10$^4$ M$^{-1}$ cm$^{-1}$. FT-IR (nujol mull), cm$^{-1}$: 3326 (w), 3264 (w), 3111 (w), 2718 (s), 1684 (s), 1647 (m), 1601 (m), 1543 (br, m), 1342 (m), 1316 (m), 1098 (s). $^1$H-NMR (δ, ppm, TMS; CD$_3$CN): 8.58 (d, $J_{r,s}$ = 4.7 Hz, 1H; H-s), 8.15 (s, 1H; H-m), 7.81 (d, $J_{c,d}$ = 8.7 Hz, 2H; H-c), 7.80 (dd, $J_{q,r}$ = 7.7 Hz, $J_{q,p}$ = 7.9 Hz, 1H; H-q), 7.68 (s, 1H; H-g), 7.68 (d, $J_{i,j}$ = 9.3 Hz, 2H; H-i), 7.63 (d, $J_{i,j}$ = 9.3 Hz, 2H; H-j), 7.57 (d, $J_{c,d}$ = 8.7 Hz, 2H; H-d), 7.54 (s, 1H; H-f), 7.34 (dd, $J_{r,s}$ = 4.7 Hz, $J_{r,q}$ = 7.7 Hz, 1H; H-r), 7.32 (d, $J_{p,q}$ = 7.9 Hz, 1H; H-p), 5.70 (s, 2H; H-n). $^{13}$C-NMR (δ, ppm, TMS; CD$_3$CN): 155.4 (C-o), 155.1 (C-u), 149.7 (C-s), 147.4 (C-b), 147.3 (C-I), 143.4 (C-h), 139.4 (C-e), 137.6 (C-q), 127.7 (C-p), 126.2 (C-j), 126.2 (C-c), 124.7 (C-a), 123.5 (C-r), 123.4 (C-k), 121.0 (C-m), 119.5 (C-d), 118.7 (C-i), 55.4 (C-n).


Compound 1: $^1$H-NMR in CD$_3$CN
Synthesis of 2\(\text{PF}_6\)

[Chemical structure diagram]

1 (0.11 g, 0.24 mmol) was dissolved in a screw capped flask with the minimum amount of 1:1 MeCN/CHCl\(_3\) mixture. Methyl iodide (3 ml, 48.17 mmol) was added to this solution and the mixture was stirred at 50°C for 24h (ESI-MS control). After this time the solvent was removed on a rotary evaporator leaving a brownish solid. The product was dissolved in a H\(_2\)O/MeCN mixture and a saturated solution of NH\(_4\)PF\(_6\) was added dropwise; solid precipitation occurs. The white product was filtered off and dried. (yield 56%, 82mg). ESI-MS (CH\(_3\)CN): \(m/z\) (+) 453 \([\text{M}]^+\). UV–vis. (CH\(_3\)CN): \(\lambda_{\text{max}} = 280 \text{ nm}, \varepsilon_{280} = 50 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\). FT-IR (nujol mull), cm\(^{-1}\): 3348 (w), 3149 (w), 3116 (w), 3073 (w), 2718 (s), 1684 (s), 1637 (m), 1601 (m), 1531 (m), 1327 (m), 1098 (s), 840 (br, s). \(^1\)H-NMR (\(\delta\), ppm, TMS; CD\(_3\)CN): 8.74 (d, \(J_{r,s} = 6.1 \text{ Hz}, 1\text{H}; H-s\)), 8.46 (false t, \(J_{\text{obs}} = 8.0 \text{ Hz}, 1\text{H}; H-q\)), 8.25 (s, 1H; H-m), 8.03 (s, 1H; H-g), 7.99 (false t, \(J_{\text{obs}} = 6.6 \text{ Hz}, 1\text{H}; H-r\)), 7.89 (s, 1H; H-f), 7.85 (d, \(J_{c,d} = 8.7 \text{ Hz}, 2\text{H}; H-c\)), 7.69 (d, \(J_{i,j} = 8.7 \text{ Hz}, 2\text{H}; H-i\)), 7.63 (d, \(J_{i,j} = 8.7 \text{ Hz}, 2\text{H}; H-j\)), 7.61 (d, \(J_{c,d} = 8.7 \text{ Hz}, 2\text{H}; H-d\)), 7.50 (d, \(J_{p,q} = 8.1 \text{ Hz}, 1\text{H}; H-p\)), 6.06 (s, 2H; H-n), 4.34 (s, 3H; H-t); \(^{13}\)C-NMR (\(\delta\), ppm, TMS; CD\(_3\)CN): 152.5 (C-u), 152.0 (C-o), 148.2 (C-b), 148.2 (C-l), 147.7 (C-s), 147.0 (C-q), 143.4 (C-h), 140.0 (C-e), 128.1 (C-p), 127.9 (C-r), 126.7 (C-j), 126.4 (C-c), 124.9 (C-a), 123.4 (C-k), 121.9 (C-m), 119.5 (C-d), 118.8 (C-i), 50.2 (C-n), 46.4 (C-t).
Compound 2·PF₆: ¹H-NMR in CD₃CN
Figure S1. (a) Absorption spectra taken over the course of the titration of a solution of 1 (3.0 × 10^{-4} M) in acetonitrile, with a 2.0 × 10^{-2} M solution of the TBA-Cl (l = 0.1 cm); (b) distribution of the species present at the equilibrium. Blue line: free receptor; red line: bound receptor; black triangles: superimposed plots of Molar Absorbance (at 290 nm) vs. eqv. of TBA-Cl. T = 25°C.

Figure S2. (a) Absorption spectra taken over the course of the titration of a solution of 2 (3.0 × 10^{-4} M) in acetonitrile, with a 2.0 × 10^{-2} M solution of the TBA-Cl (l = 0.1 cm); (b) distribution of the species present at the equilibrium. Blue line: free receptor; red line: bound receptor; black triangles: superimposed plots of Molar Absorbance (at 290 nm) vs. eqv. of TBA-Cl. T = 25°C.
Figure S3. (a) Absorption spectra taken over the course of the titration of a solution of 1 \((1.7 \times 10^{-4} \text{ M})\) in acetonitrile, with a \(2.7 \times 10^{-2} \text{ M}\) solution of the TBA-H2PO4 \((l = 0.1 \text{ cm})\); (b) distribution of the species present at the equilibrium. Blue line: free receptor; red line: bound receptor; superimposed plots of Molar Absorbance (at 292 nm, red triangles; at 270 nm, white triangles) vs. eqv. of TBA-H2PO4. \(T = 25^\circ\text{C}\).

Figure S4. Absorption spectra taken over the course of the titration of a solution of 2 \((1.7 \times 10^{-4} \text{ M})\) in acetonitrile, with a \(2.7 \times 10^{-2} \text{ M}\) solution of the DBU \((l = 0.1 \text{ cm})\). Inset figure: plot of Molar Absorbance at 400 nm (black triangles) vs. eqv. of DBU. \(T = 25^\circ\text{C}\).
Figure S5. $^1$H-NMR spectra taken over the course of the titration of a $5.2 \times 10^{-3}$ M solution of 1 in CD$_3$CN, with a 0.13 M solution of the TBA-Cl. Spectra 1-7 correspond to the addition of 0, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0 eqv. of TBA-Cl, respectively.

Figure S6. (a) $^1$H-NMR spectra taken over the course of the titration of a $9.7 \times 10^{-3}$ M solution of 1 in CD$_3$CN, with a 0.069 M solution of the TBA-H$_2$PO$_4$. Spectra 1-9 correspond to the addition of 0, 0.2, 0.4, 0.6, 0.8, 0.9, 1.0, 2.5 and 4.5 eqv. of TBA-H$_2$PO$_4$, respectively. (b) Plot of $\Delta \delta_{H5}$ vs. eqv. of the added TBA-H$_2$PO$_4$. 
Figure S7. $^1$H-NMR spectra taken over the course of the titration of a $3.5 \times 10^{-3}$ M solution of 2 in CD$_3$CN, with a 0.13 M solution of the TBA-Cl. Spectra 1-5 correspond to the addition of 0, 0.5, 1.0, 1.5 and 2.0 eqv. of TBA-Cl, respectively.
Figure S8. (a) Family of UV-vis. spectra taken over the course of the pH-spectrophotometric titration of 2 in CH$_3$CN/water mixture (9/1 v/v). (b) Distribution diagram with the superimposed pH-spectrophotometric profile (at 400 nm).

Figure S9. A simplified sketch of overlapping receptors 1 forming rows parallel to the direction of the $a$ crystallographic axis. These rows are maintained by weak N-H···O urea-urea interactions (atom names identify the independent N-H···O interaction). Features of the N-H···O interactions are: N(1)···O(1)' 3.18(1) Å, H(1N)···O(1)' 2.37(3) Å, N(1)-H(1N)···O(1)' 142.3(23)°; symmetry code: ('') = x-1/2, 1/2-y, z.