Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

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

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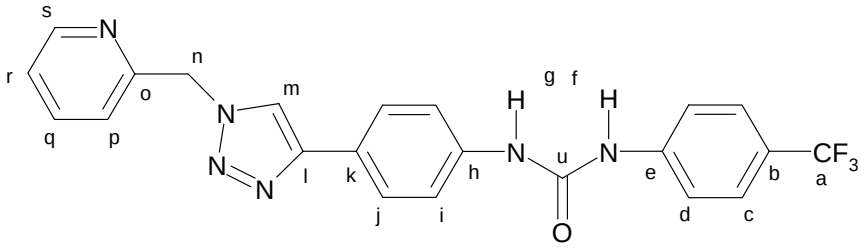
Synthesis of 1

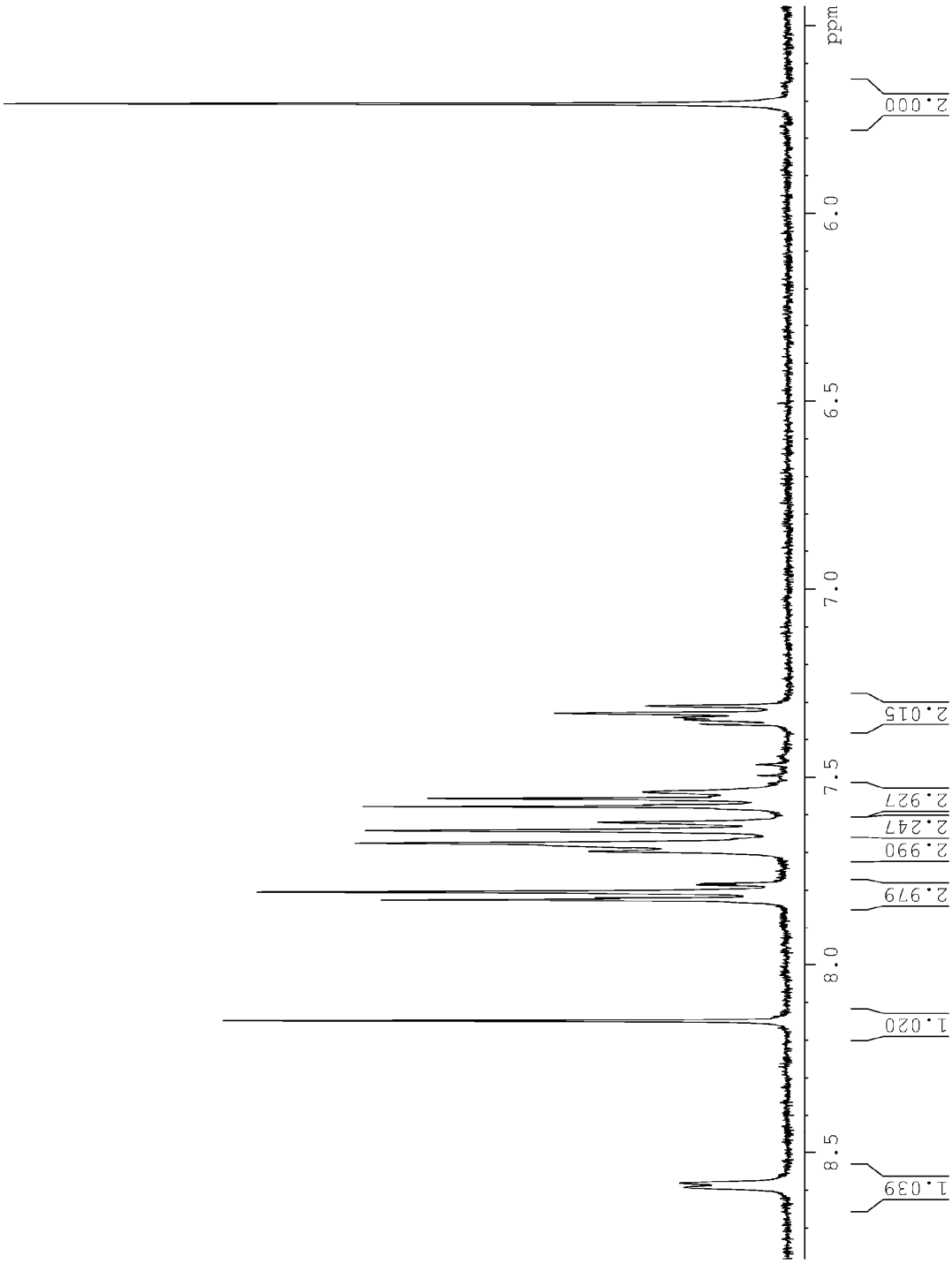


To a solution of alkyne, N-(4-trifluoromethylphenyl)-N'-(4'-ethynylphenyl)urea, (0.35 g, 1.30 mmol) and 2-(azidomethyl)pyridine[1-2] (0.21 g, 1.52 mmol) in 20 ml methanol/t-butanol 1:1 (v:v) mixture was added a solution of $Cu(OAc)_2 \cdot H_2O$ (13 mg, 0.065 mmol) in 1 ml of water. The reaction mixture was stirred at room temperature. After 18 h stirring, a white precipitate was filtered out (yield 80%, 0.45 g). ESI-MS (CH_3CN): *m/z* (–) 473 $[M + Cl]^-$; UV–vis. (CH_3CN): λ_{max} = 282 nm, $\varepsilon_{282} = 52 \times 10^4\ M^{-1}\ cm^{-1}$. 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_3CN): 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_3CN): 155.4 (C-o), 155.1 (C-u), 149.7 (C-s), 147.4 (C-b), 147.3 (C-l), 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).

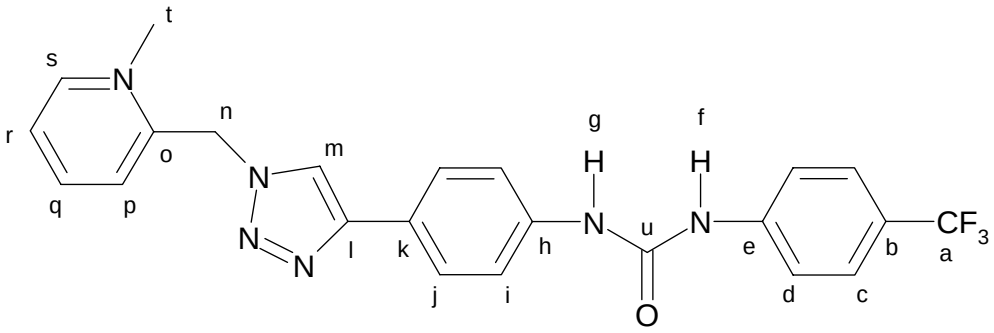
[1] W. S. Brotherton, H. A. Michaels, J. T. Simmons, R. J. Clark, N. S. Dalal, and L. Zhu, *Org. Lett.*, **2009**, *11*, 4954-4957. D. Urankar, B. Pinter, A. Pevec, F. De Proft, I. Turel, J. Kosmrlj, Inorg. Chem. 2010, 49, 4820–4829

[2] J. Ritschel, F. Sasse and M. E. Maier**,** *Eur. J. Org. Chem.* **2007**, 78-87.

Compound 1: ^{1}H-NMR in CD_3CN

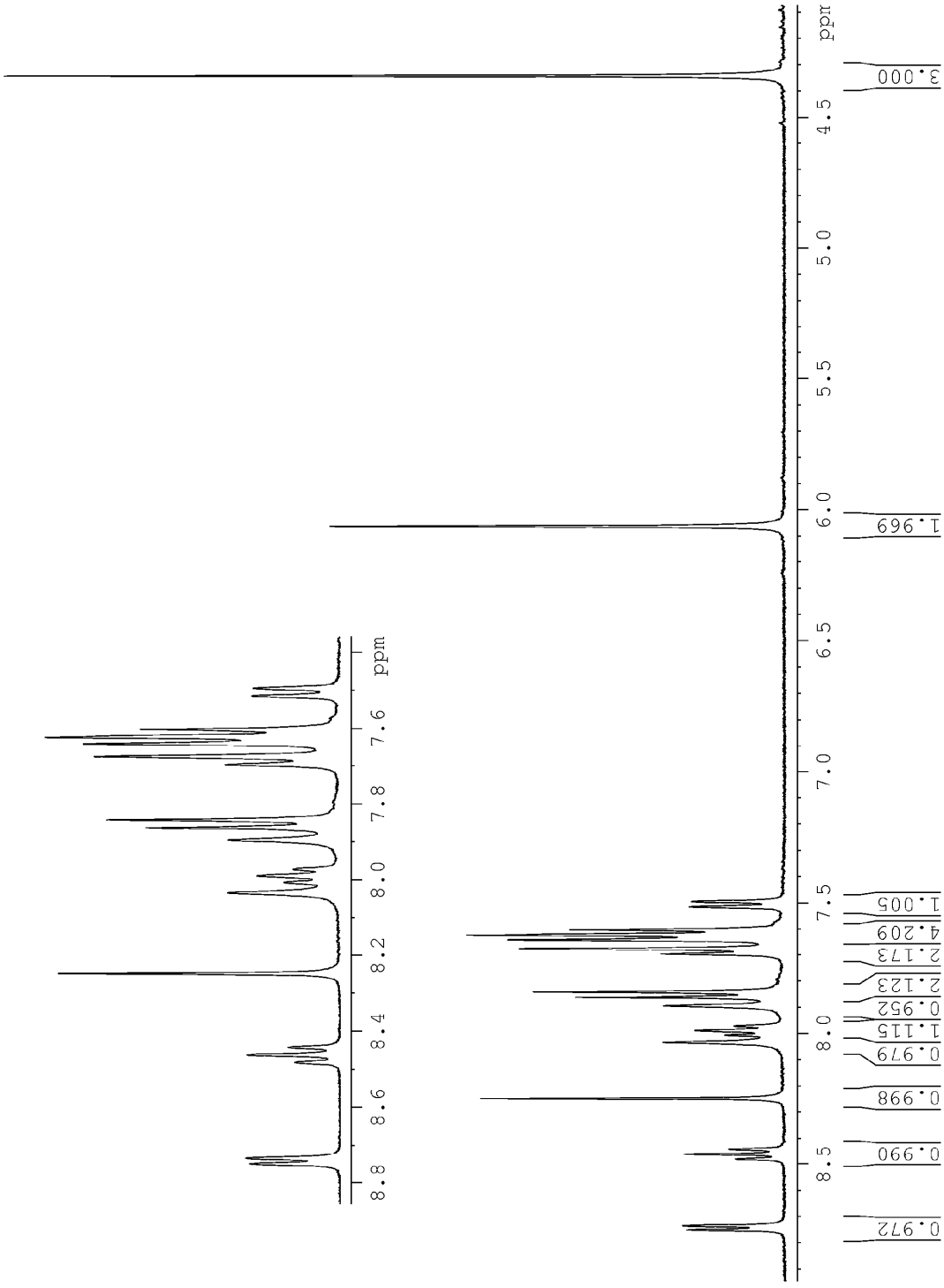


Synthesis of $2 \cdot PF_6$



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_2O/MeCN mixture and a saturated solution of NH_4PF_6 was added dropwise; solid precipitation occurs. The white product was filtered off and dried. (yield 56%, 82mg). ESI-MS (CH_3CN): *m/z* (+) 453 $[M]^+$. UV–vis. (CH_3CN): λ_{max} = 280 nm, $\varepsilon_{280} = 50 \times 10^4\ M^{-1}\ cm^{-1}$. 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 (δ, ppm, TMS; CD_3CN): 8.74 (d, $J_{r,s}$ = 6.1 Hz, 1H; H-s), 8.46 (false t, J_{obs} = 8.0 Hz, 1H; H-q), 8.25 (s, 1H; H-m), 8.03 (s, 1H; H-g), 7.99 (false t, J_{obs} = 6.6 Hz, 1H; H-r), 7.89 (s, 1H; H-f), 7.85 (d, $J_{c,d}$ = 8.7 Hz, 2H; H-c), 7.69 (d, $J_{i,j}$ = 8.7 Hz, 2H; H-i), 7.63 (d, $J_{i,j}$ = 8.7 Hz, 2H; H-j), 7.61 (d, $J_{c,d}$ = 8.7 Hz, 2H; H-d), 7.50 (d, $J_{p,q}$ = 8.1 Hz, 1H; H-p), 6.06 (s, 2H; H-n), 4.34 (s, 3H; H-t); ^{13}C-NMR (δ, ppm, TMS; CD_3CN): 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·PF_6: ^{1}H-NMR in CD_3CN



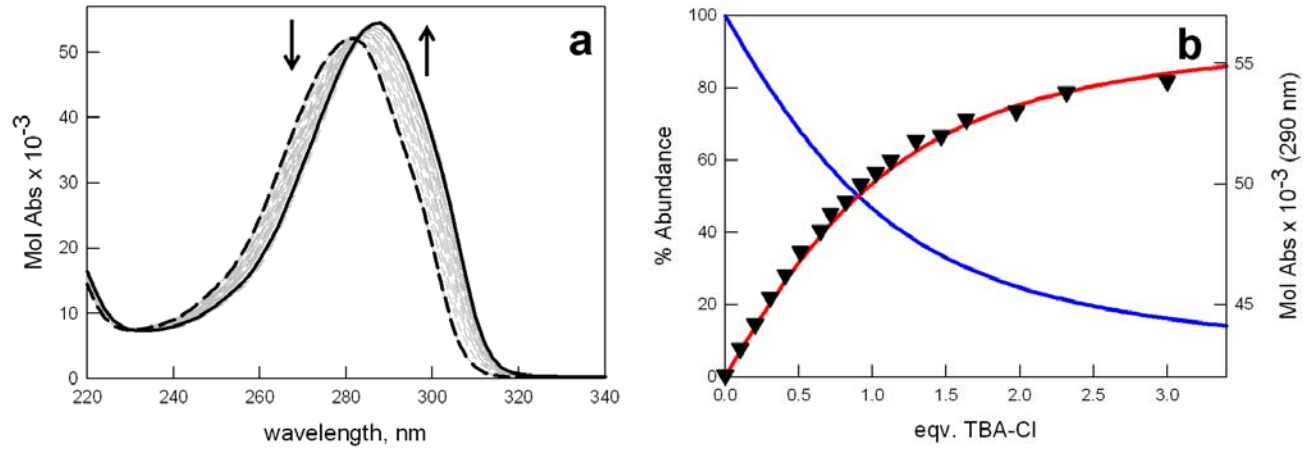


Figure S1. (a)Absorption spectra taken over the course of the titration of a solution of **1** (3.0×10^{-4} M) in acetonitrile, with a 2.0×10^{-2} M solution of the TBA-Cl (l = 0.1 cm); (b) distribution of the species present at the equilibrium. Blue line: free receptor; red line: bound receptor; black triangles: superimposed plots of Molar Absorbance (at 290 nm) *vs.* eqv. of TBA-Cl. T = 25°C.

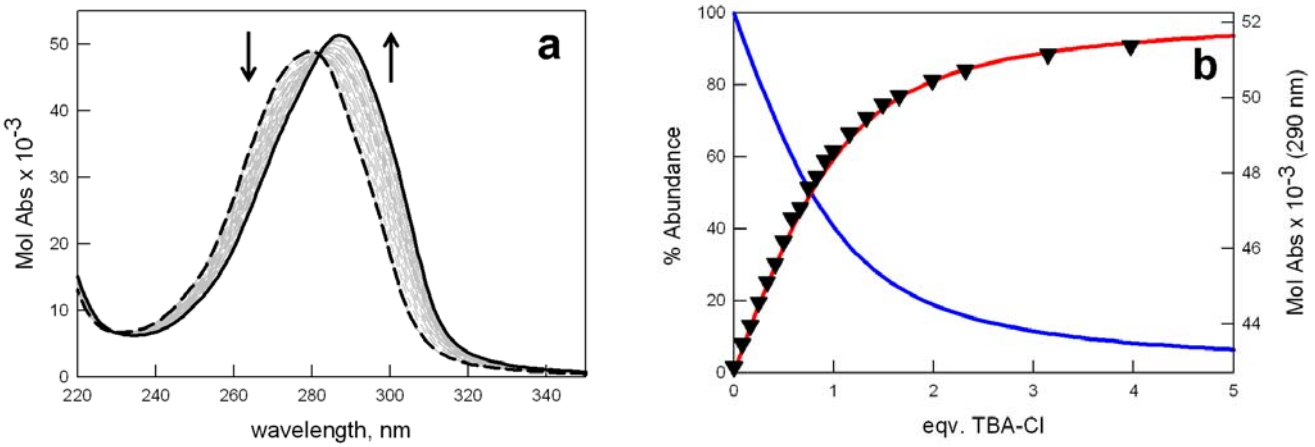


Figure S2. (a)Absorption spectra taken over the course of the titration of a solution of **2** (3.0×10^{-4} M) in acetonitrile, with a 2.0×10^{-2} M solution of the TBA-Cl (l = 0.1 cm); (b) distribution of the species present at the equilibrium. Blue line: free receptor; red line: bound receptor; black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

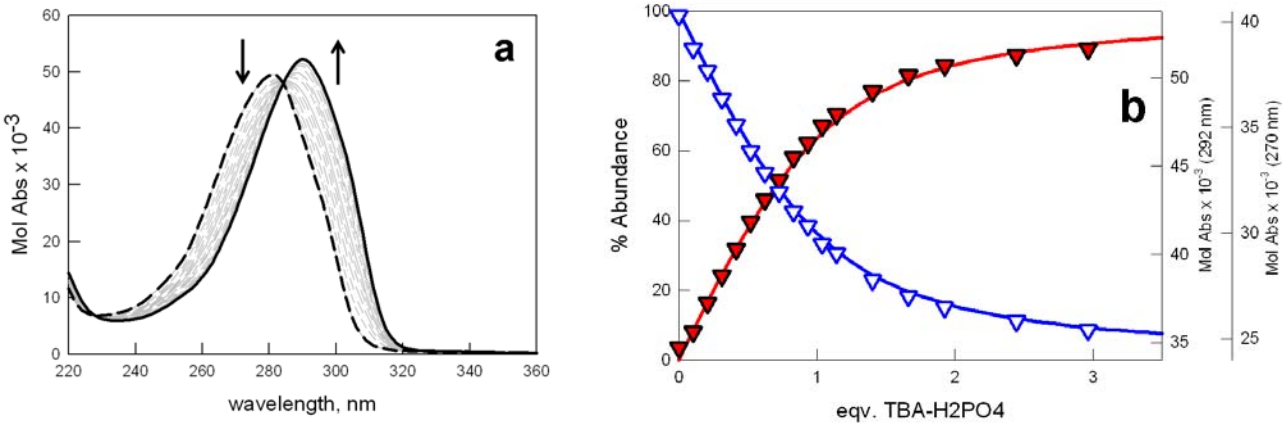


Figure S3. (a)Absorption spectra taken over the course of the titration of a solution of **1** (1.7×10^{-4} M) in acetonitrile, with a 2.7×10^{-2} M solution of the TBA-H_2PO_4 (l = 0.1 cm); (b) distribution of the species present at the equilibrium. Blue line: free receptor; red line: bound receptor; superimposed plots of Molar Absorbance (at 292 nm, red triangles; at 270 nm, white triangles) *vs.* eqv. of TBA-H_2PO_4. T = 25°C.

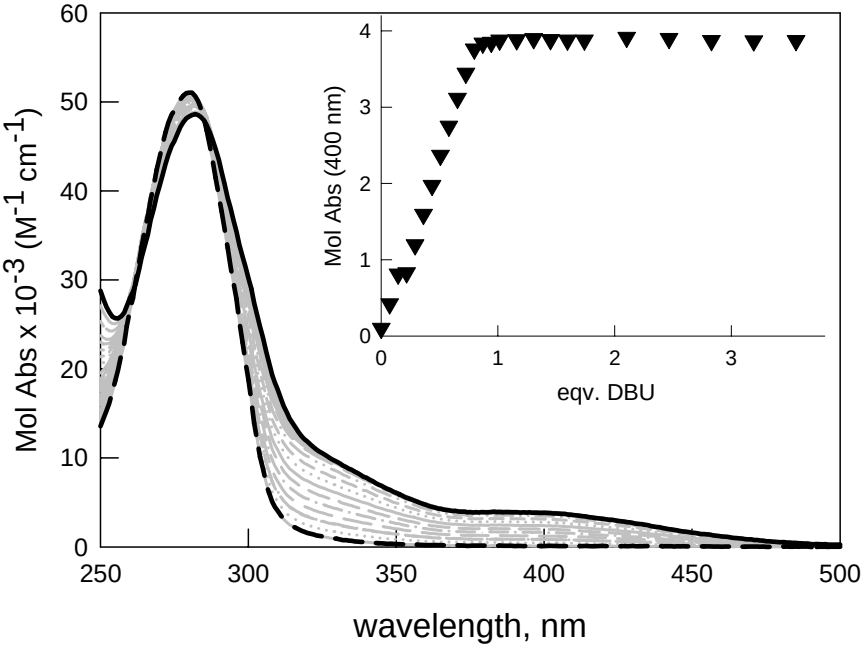


Figure S4. Absorption spectra taken over the course of the titration of a solution of **2** (1.7×10^{-4} M) in acetonitrile, with a 2.7×10^{-2} M solution of the DBU (l = 0.1 cm). Inset figure: plot of Molar Absorbance at 400 nm (black triangles) *vs.* eqv. of DBU. T = 25°C.

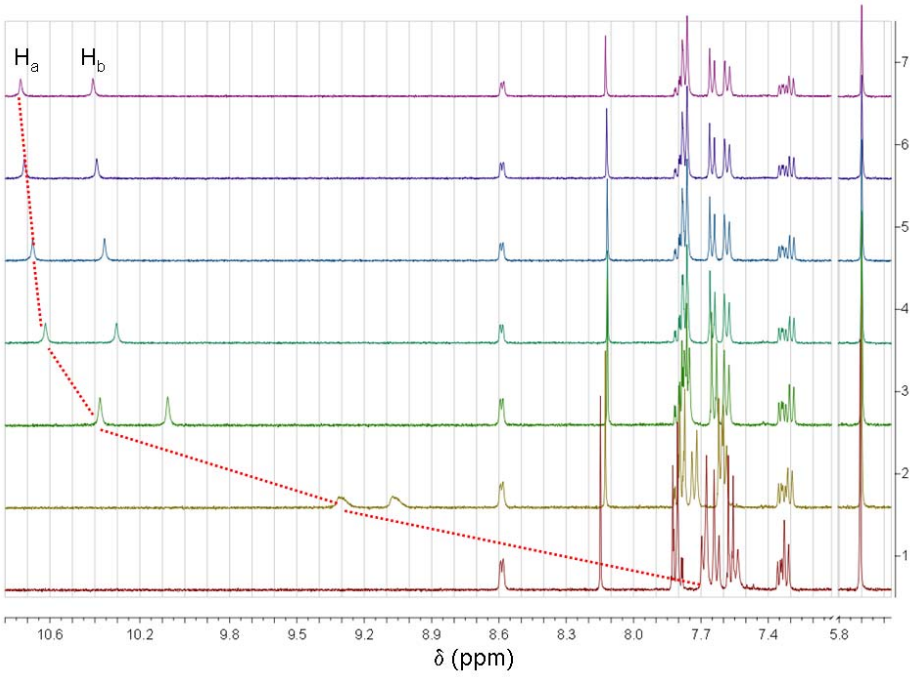


Figure S5. ^{1}H-NMR spectra taken over the course of the titration of a 5.2×10^{-3} M solution of **1** in CD_3CN, with a 0.13 M solution of the TBA-Cl. Spectra 1-7 correspond to the addition of 0, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0 eqv. of TBA-Cl, respectively.

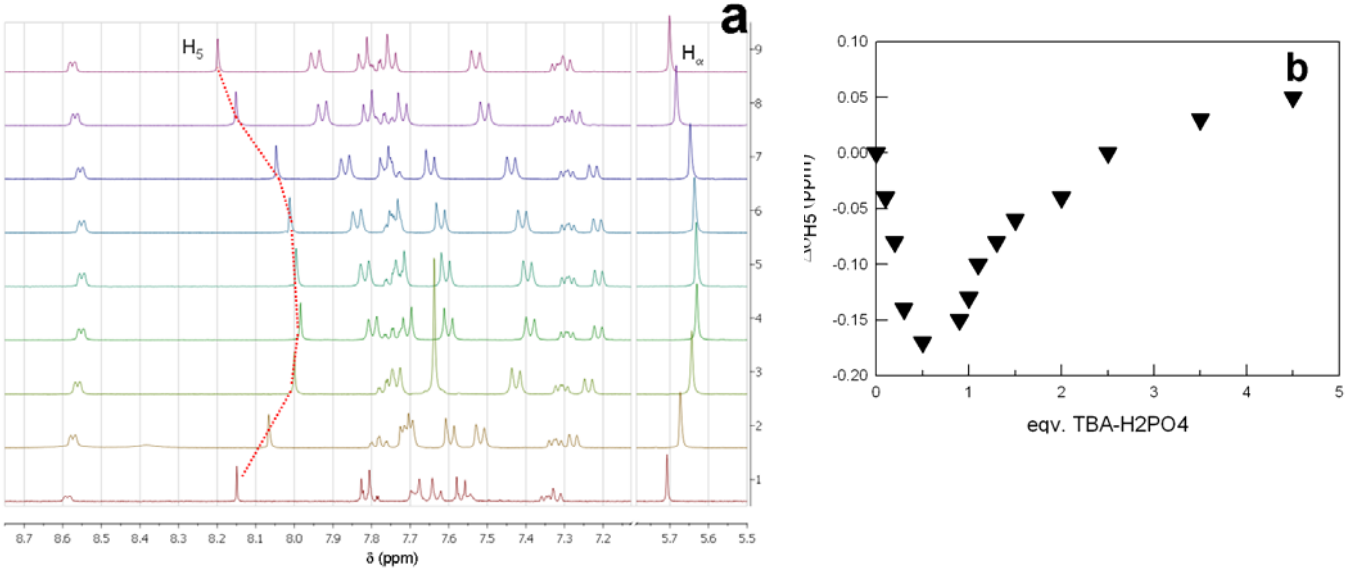


Figure S6. (a) ^{1}H-NMR spectra taken over the course of the titration of a 9.7×10^{-3} M solution of **1** in CD_3CN, with a 0.069 M solution of the TBA-H_2PO_4. Spectra 1-9 correspond to the addition of 0, 0.2, 0.4, 0.6, 0.8, 0.9, 1.0, 2.5 and 4.5 eqv. of TBA-H_2PO_4, respectively. (b) Plot of $\Delta\delta H_5$ vs. eqv. of the added TBA-H_2PO_4.

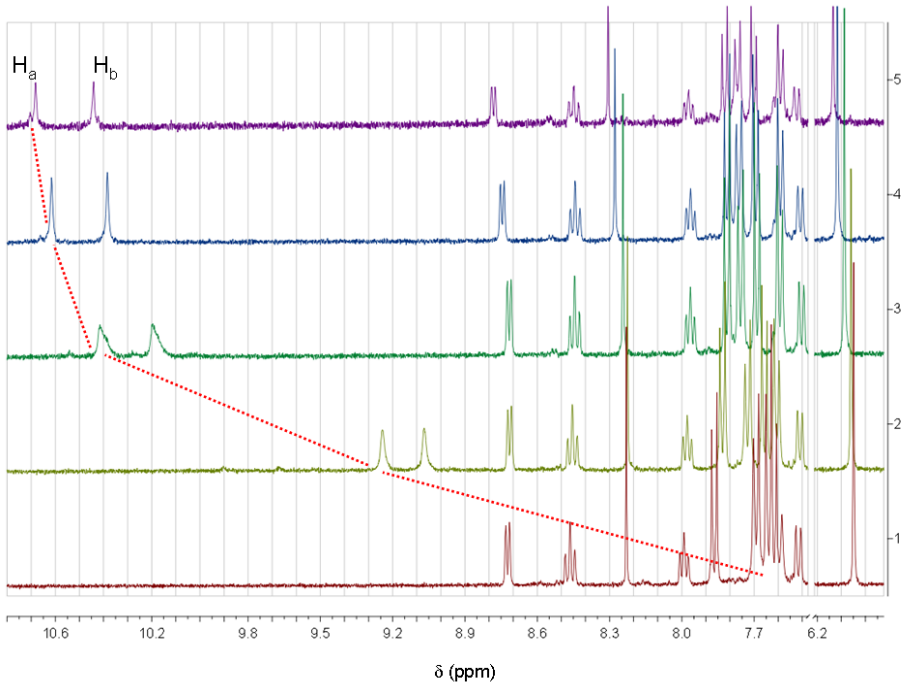


Figure S7. ^{1}H-NMR spectra taken over the course of the titration of a 3.5×10^{-3} M solution of **2** in CD_3CN, with a 0.13 M solution of the TBA-Cl. Spectra 1-5 correspond to the addition of 0, 0.5, 1.0, 1.5and 2.0 eqv. of TBA-Cl, respectively.

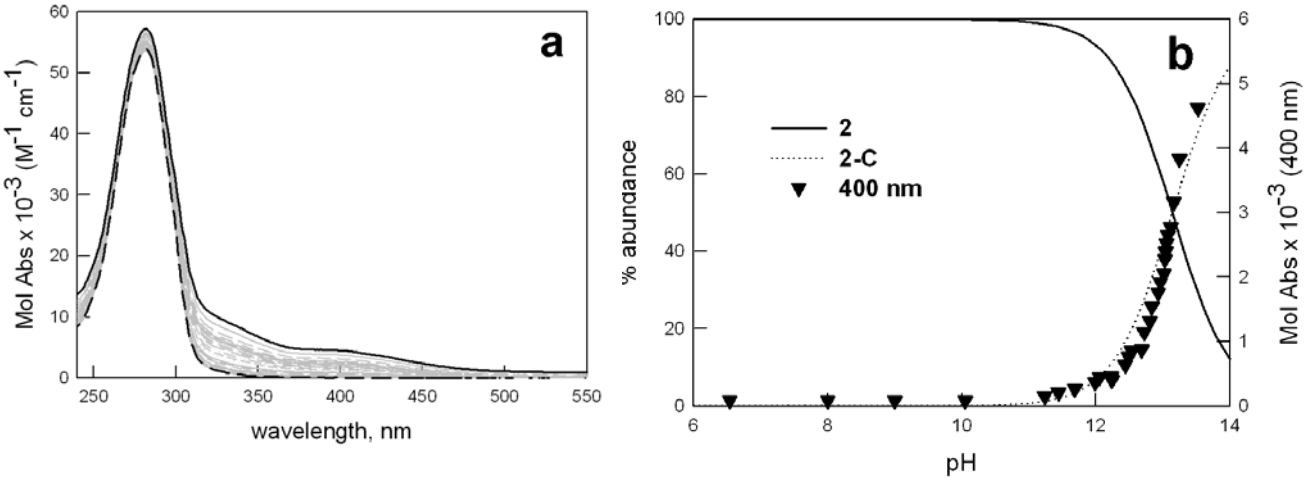


Figure S8. (a) Family of UV-vis. spectra taken over the course of the pH-spectrophotometric titration of **2** in CH_3CN/water mixture (9/1 v/v). (b) Distribution diagram with the superimposed pH-spectrophotometric profile (at 400 nm).

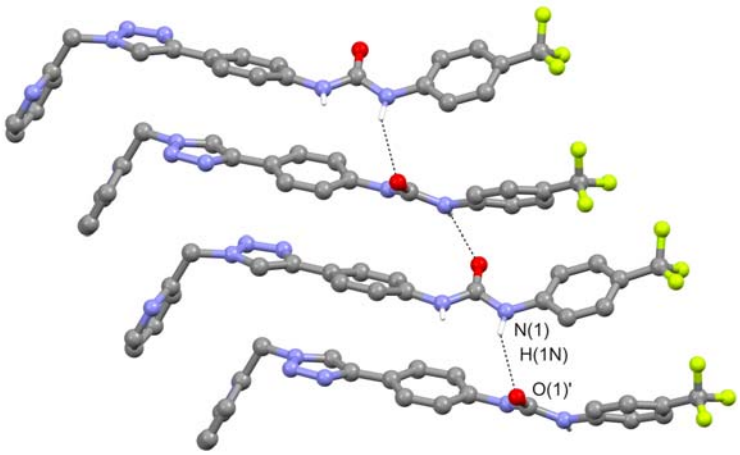


Figure S9. A simplified sketch of overlapping receptors **1** forming rows parallel to the direction of the *a* crystallographic axis. These rows are maintained by weak N-H···O urea-urea interactions (atom names identify the independent N-H···O interaction). Features of the N-H···O interactions are: 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*.