Supporting Information

New Host-Guest Chemistry of Supramolecular Nanotubes

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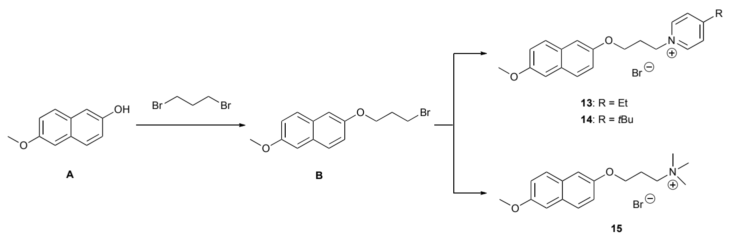
Contents:

General

All solvents were of reagent grade quality (DMF, CH_3CN) or HPLC grade ($CHCl_3$) and purchased commercially. All starting materials were purchased from Aldrich or Fluka and used without further purification. NMR spectra were recorded on Bruker DRX 400 MHz or 500 MHz instruments. The NMR spectra were referenced to solvent and the spectroscopic solvents were purchased from Euriso-Top (C. E. Saclay). All the spectra were recorded at 298K. All high-resolution (HR) electrospray ionization (ESI) mass spectra were recorded on a Waters LCT Premier XE instrument. The CD and UV-Vis analyses were performed on an Applied Photophysics Chirascan circular dichroism spectrometer.

Synthesis of donor-acceptor systems 13 and 14 and ammonium ion 15.



2-(3-Bromopropyloxy)-6-methoxynaphthalene B was obtained from commercially available 6-methoxy-2-naphthol and 1,3-dibromopropane following the procedure reported by Mori et *al*[1].

4-ethyl-1-(3-(6-methoxynaphthalen-2-yloxy)propyl)pyridinium bromide (13). To a solution of **B** (295 mg, 1 mmol) in DMF/ACN (5 ml, 1:1) was added 4-ethylpyridine (170 µL, 1.5 mmol) and the solution was stirred at 90°C for 16 h. The solvent was removed under reduced pressure, the residue was dissolved in EtOAc (20 mL) and washed with water (2 x 20 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo to give the desired product as a light brown solid (53% yield). ^{1}H MNR ($CDCl_3$, 400 MHz): δ = 9.26 (d, *J* = 6.0 Hz, 2H), 7.68 (d, *J* = 5.6 Hz, 2H), 7.52 (dd, *J* = 8.8 and 2.0 Hz, 2H), 7.05 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hx, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.8 and 2.4 Hz, 1H), 5.17 (t, *J* = 6.6 Hz, 2H), 4.11 (t, *J* = 5.2 Hz, 2H), 3.82 (s, 3H), 2.83 (q, *J* = 7.6 Hz, 2H), 2.65-2.52 (m, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.3, 156.7, 154.7, 145.1, 130.2, 129.8, 128.6, 128.5, 127.5, 119.4, 118.7, 107.5, 106.3, 64.8, 58.9, 55.7, 31.4, 29.2, 13.6; HRMS (ESI) calcd. for $C_{21}H_{24}NO_2^+$ $[M]^+$ (*m/z*): 322.1802, found: 322.1870.

4-*tert*-butyl-1-(3-(6-methoxynaphthalen-2-yloxy)propyl)pyridinium bromide (14). To a solution of **B** (147 mg, 0.5 mmol) in DMF/ACN (5 ml, 1:1) was added 4-*tert*-butylpyridine (67 mg, 0.5 mmol) and the solution was stirred at 90°C for 16 h. The solvent was removed under reduced pressure to give a pale yellow glue. The target product was obtained as a white solid after crystallization from EtOH. ^{1}H MNR ($CDCl_3$, 400 MHz): δ = 9.47 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.08 (dd, *J* = 8.8 and 2.4 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.8 ans 2.4 Hz, 1H), 5.23 (t, *J* = 7.0 Hz, 2H), 4.19 (t, *J* = 5.6 Hz, 2H), 3.80 (s, 3H), 2.60-2.50 (m, 2H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.3, 156.7, 154.6, 145.1, 130.3, 129.9, 128.7, 128.6, 125.4, 107.7, 106.4, 64.8, 58.9, 55.7, 36.9, 31.4, 30.4; HRMS (ESI) calcd. for $C_{23}H_{28}NO_2^+$ $[M]^+$ (*m/z*): 350.2120, found: 350.2122.

3-(6-methoxynaphthalen-2-yloxy)-*N*,*N*,*N*-trimethylpropan-1-aminium bromide (15). To a solution of **B** (147 mg, 0.5 mmol) in acetone (5 mL) was added trimethylamine (33% w/w solution in EtOH, 300 μL) and the solution was stirred at room temperature for 18 h. The white precipitate formed was filtered, washed with acetone and dried in vacuo to give **15** in 75% yield. ^{1}H MNR (DMSO-*d6*, 400 MHz): δ = 7.78 (t, *J* = 9.6 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 2.8 Hz, 1H), 7.22-7.15 (m, 2H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 3.62-3.46 (m, 2H), 3.17 (s, 9H), 2.26-2.22 (m, 2H; ^{13}C NMR (DMSO-*d6*, 100 MHz): δ = 156.2, 154.8, 129.9, 129.7, 128.6, 128.5, 119.2, 119.0, 107.7, 106.5, 65.1, 63.4, 55.5, 52.7, 22.9; HRMS (ESI) calcd. for $C_{17}H_{24}NO_2^+$ $[M]^+$ (*m/z*): 274.1802, found: 274.1845.

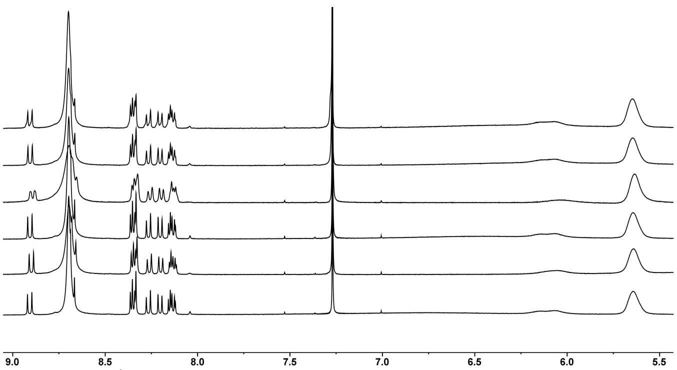


Figure S1. ^{1}H NMR spectra of a solution containing **2** + **8** upon addition of increasing quantities of MeOH. From the bottom: 0%, 0.25%, 0.5%, 0.75%, 1%, 2% MeOH.

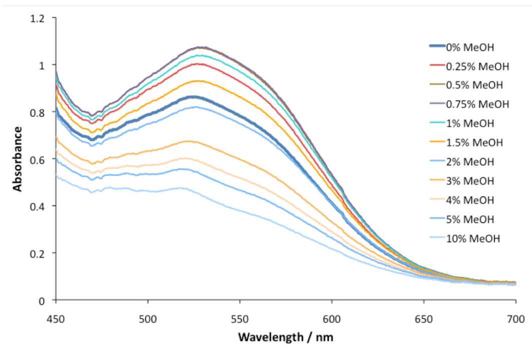


Figure S2. UV-Vis spectra of **2**+**5** upon addition of MeOH

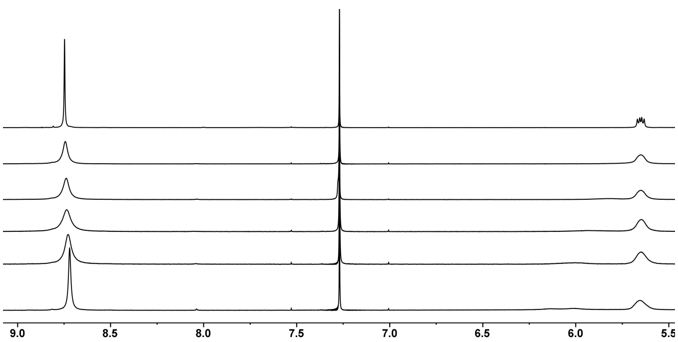


Figure S3. Addition of MeOH to a solution of **2** in $CDCl_3$. From the bottom: 0%, 0.25%, 0.5%, 0.75%, 1% and 2% MeOH

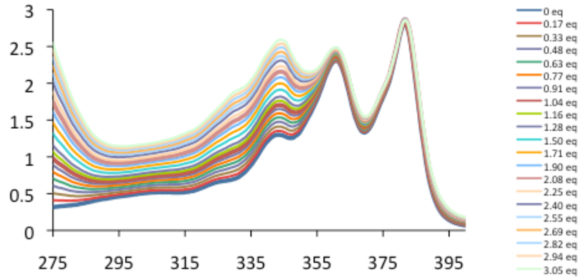


Figure S4. UV-Vis spectra of **2** titrated with a solution of **13** in $CHCl_3$

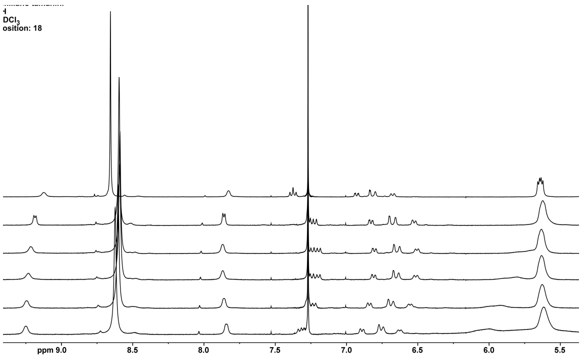


Figure S5. Addition of MeOH to a solution of **2** + **13** in $CDCl_3$. From the bottom: 0%, 0.25%, 0.5%, 0.75%, 1% and 2% MeOH

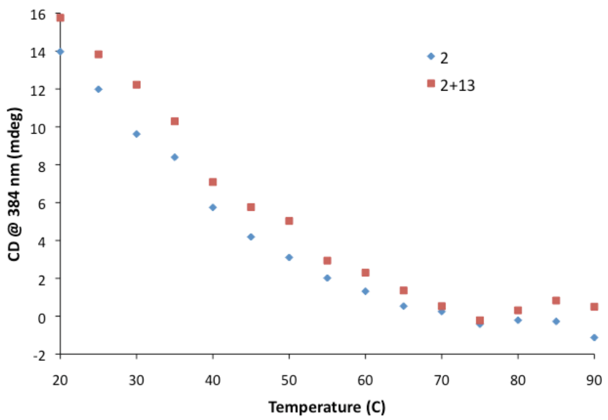


Figure S6. Melting curves of a solution of **2** and a mixture **2** + **13** in tetrachloroethane

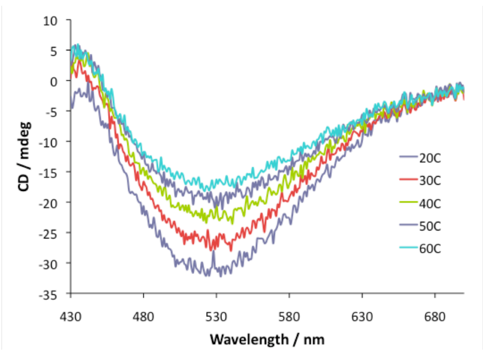


Figure S7. CD spectra of a solution containing **2** + **13** at different temperatures: 20, 30, 40, 50, and 60°C.

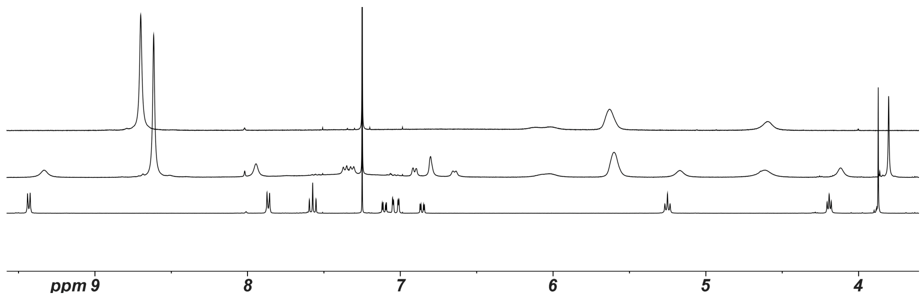


Figure S8. ^{1}H NMR spectra of (from the bottom) **14**, **2**+**14** and **2** in $CDCl_3$

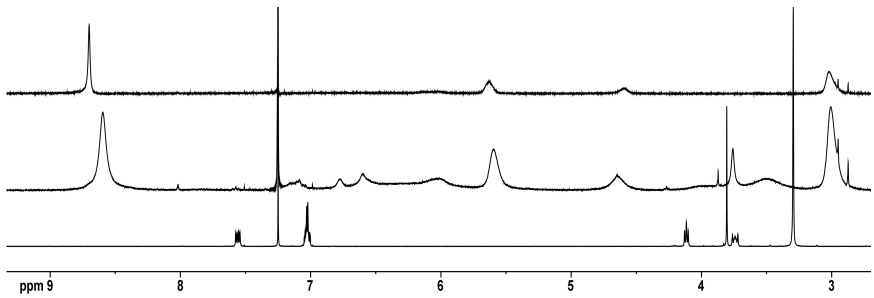


Figure S9. ^{1}H NMR spectra of (from the bottom) **15** (in $CDCl_3/CD_3CN$), **2**+**15** and **2** in $CDCl_3$

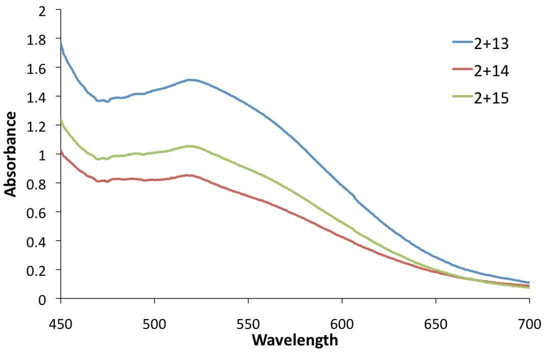


Figure S10. UV-Vis spectra of **2**+**13**, **2**+**14** and **2**+**15** in $CHCl_3$.

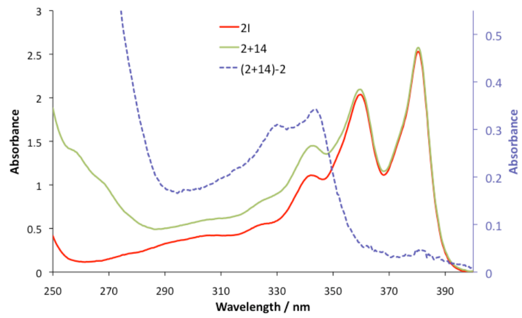


Figure S11. UV-Vis spectra of **2** and a mixture **2**+**14** (1:1 ratio) and the contribution of **14** to the **2**+**14** solution (dotted line).

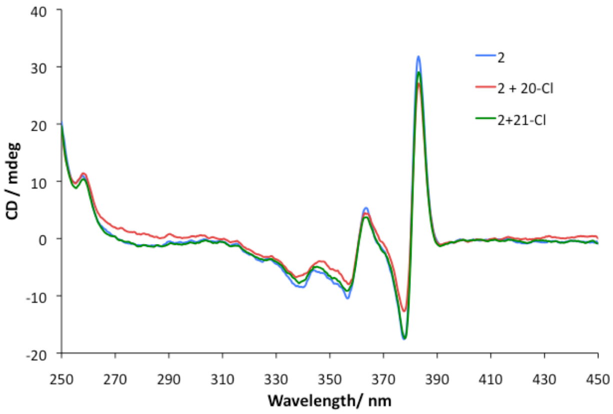


Figure S12. CD spectra of **2** upon addition of acetylcholine chloride (**20·Cl)** and **21·Cl**.

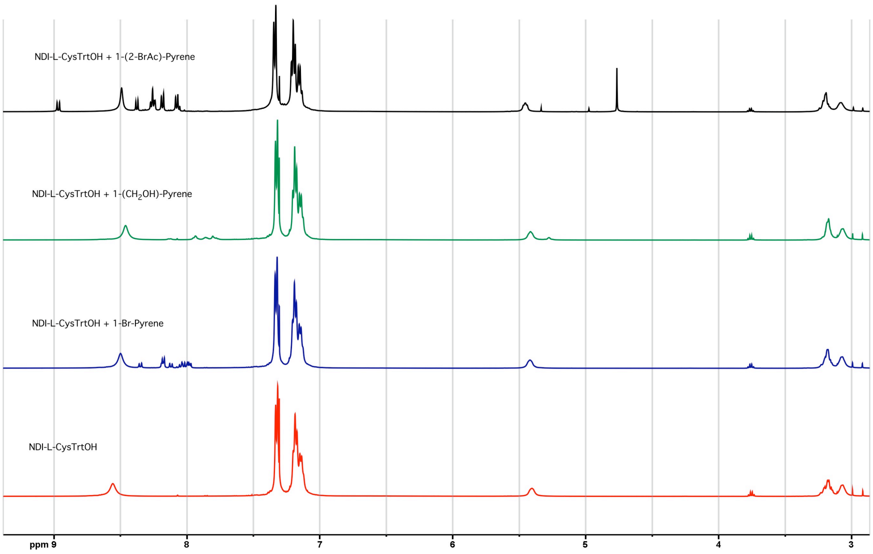


Figure S13. ^{1}H-NMR spectra (bottom to top) of 1:2 mixtures of **1** + **6**, **7**, and **9**, in $CDCl_3$.

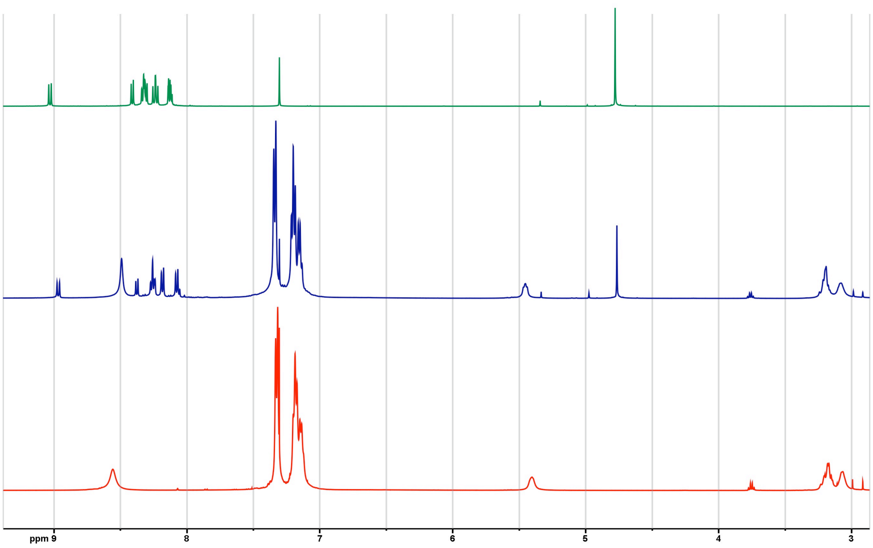


Figure S14. ^{1}H-NMR spectra (bottom to top) of **1**, **1 + 9** (1:2 mixture), **9** in $CDCl_3$

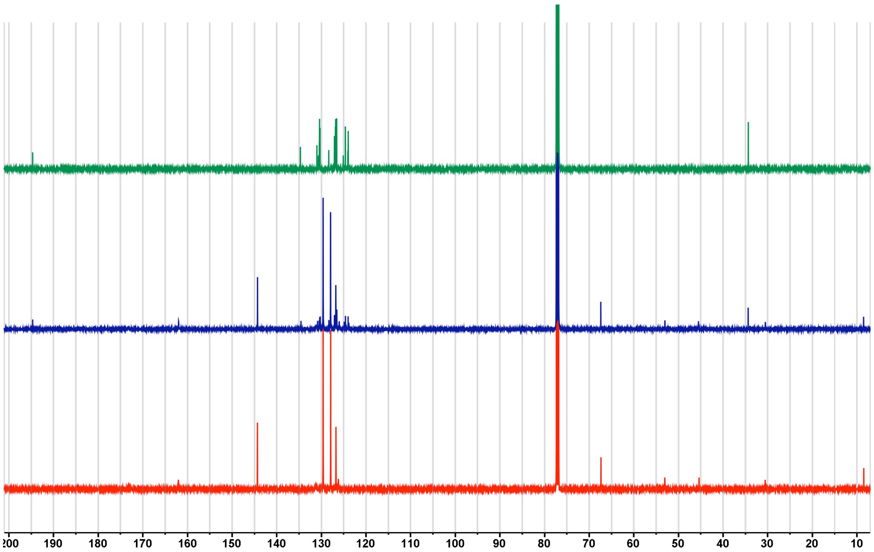


Figure S15. ^{13}C-NMR spectra (bottom to top) of **1**, **1** + **9** (1:2 mixture), **9** in $CDCl_3$

Figure S16. ^{13}C-NMR spectra (bottom to top) of **1**, **1** + **9** (1:2 mixture), **9** in $CDCl_3$ (zoom)

References

1. T. Mori, Y. H. Ko, K. Kim, I. Inoue, *J. Org. Chem.*, 2006, **71**, 3232.