Measuring the Stability of Supramolecular Complexes in the Proximity of Single-Walled Carbon Nanotubes

Teresa Naranjo, Julia Villalva, and Emilio M. Pérez*© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made. An invited contribution to a Special Collection dedicated to Functional Supramolecular Systems
## Supporting Information

### Contents

| Section | Title                                                                 | Page |
|---------|-----------------------------------------------------------------------|------|
| S1.     | Materials and methods                                                  | 2    |
|         | a) Chemicals and reagents                                             | 2    |
|         | b) Equipment                                                           | 2    |
| S2.     | Synthesis of the Hamilton receptor-cyanuric acid derivative pair (HR-cy) | 2    |
|         | a) Cy synthesis                                                        | 2    |
|         | b) HR synthesis                                                        | 10   |
| S3.     | Synthesis of the Ammonium derivative (Am)                              | 16   |
| S4.     | SWNTs functionalization                                                | 21   |
| S5.     | Procedure for the UV/Vis titration experiments                         | 21   |
|         | a) Example of UV/Vis titration experiment for the HR vs Cy couple      | 22   |
|         | b) Example of UV/Vis titration experiment for the 18-Crown-6 vs Am couple | 23   |
| S6.     | TGA titration experiments procedure                                    | 25   |
|         | a) Thermogravimetric plots                                             | 26   |
| S7.     | References                                                             | 27   |
S1. Materials and methods

a) Chemicals and reagents

All solvents were dried according to standard procedures. Reagents were used as purchased. The 4'-Aminobenzo-18-crown-6 was directly purchased from Aldrich (CAS: 68941-06-0) and used without further modification. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh, or Scharlau 60, 230-240 mesh). Analytical thin layer chromatographies (TLC) were performed using aluminium-coated Merck Kieselgel 60 F254 plates. Fast Atom Bombardment (FAB) and Matrix-assisted Laser desorption ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a VS AutoSpec spectrometer and a Bruker ULTRAFLEX III spectrometer, respectively.

The SWNTs employed were plasma-purified SWNTs (pp-SWNTs, 98% purity, 0.8–1.6 nm in diameter).

b) Equipment

NMR

NMR spectra were recorded on a BrukerAvance 400 (H: 400 MHz, 13C: 101 MHz) at 298 K using the solvent noted in each case. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad.

Mass spectrometry

Fast Atom Bombardment (FAB) and Matrix-assisted Laser desorption ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a VS AutoSpec spectrometer and a Bruker ULTRAFLEX III spectrometer, respectively.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed using a TA Instruments TGAQ500 with a ramp of 10 °C·min⁻¹ under air or nitrogen from 50 to 1000 °C.

UV/Vis spectroscopy

UV/Vis experiments were performed on a Varian Cary® 50 UV/Vis spectrometer.

S2. Synthesis of the Hamilton receptor-cyanuric acid derivative pair (HR-cy)

a) Cy synthesis
5-bromopentanoyl chloride (1). 5-Bromovaleric acid (200 mg, 1.1 mmol) was suspended in anhydrous DCM (4.4 mL), 2 drops of DMF were added and oxalyl chloride (0.12 mL, 1.4 mmol) was added dropwise over a period of 15 min. The reaction was stirred for two hours, then the solvent was removed under reduced pressure and the crude material was directly used in the next step reaction without further purification.

N-[(2,2'-bipyridin)-4-yl]-5-bromopentanamide (2). A solution of 1 (219 mg, 1.1 mmol) in dry THF (4.5 mL) was added dropwise to a solution of [2,2'-bipyridin]-4-amine (179 mg, 1.05 mmol) and TEA (0.17 mL, 1.26 mmol) in dry THF (4.5 mL) at 0°C under Ar atmosphere. The solution was stirred at r.t. overnight. Then, a white residue was filtered off and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (DCM/MeOH 15/1) gave 2 as a yellow oil, 250 mg, 68% yield. 1H NMR (CDCl₃) δ (ppm): 8.64 (d, 1H, J = 4.6 Hz, H₂a), 8.55 (d, 1H, J = 5.7 Hz, H₂f), 8.49 (s, 1H, NH), 8.40 (d, 1H, J = 2.0 Hz, H₂g), 8.33 (d, 1H, J = 8.0 Hz, H₂h), 8.01 (dd, 1H, J = 2.0, 5.7 Hz, H₂j), 7.83 (dt, 1H, J = 1.7, 7.7 Hz, H₂i), 7.34 (ddd, 1H, J = 0.8, 4.8, 7.4 Hz, H₁j), 3.44 (t, 2H, J = 6.2 Hz, CH₂H₂j), 2.52 (t, 2H, J = 7.2 Hz, CH₂H₂k); 13C NMR (CDCl₃) δ (ppm): 172.2, 154.9, 153.4, 149.3, 148.3, 148.1, 137.4, 124.6, 121.4, 113.9, 110.8, 44.5, 36.7, 33.1, 23.6.
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

Grease
**N-((2,2'-bipyridin)-4-yl)-5-(2,4,6-trioxo-1,3,5-triazinan-1-yl)pentanamide (3).** To a solution of cyanuric acid (309 mg, 2.39 mmol) in DMF (5 mL) was added 2 (200 mg, 0.60 mmol) and 1,8-diazabicycloundec-7-ene (95 mg, 2.39 mmol). The reaction mixture was heated under 70 °C overnight, poured into the water, and extracted with ethyl acetate. The organic layer was washed with water to eliminate the excess of cyanuric acid, dried with MgSO$_4$, and filtered. The solvent was removed under reduced pressure and the crude material was purified by column chromatography using DCM : MeOH 15:1 as eluent to give 3 as a white solid; 596 mg, 25%.  

$^1$H NMR (DMSO-$d_6$) $\delta$ (ppm): 11.35 (br s, 2H, NH$_{-}$cy), 10.41 (s, 1H, NH-amide), 8.68 (d, 1H, $J$ = 4.0 Hz, H$_g$), 8.61 (d, 1H, $J$ = 2.0 Hz, H$_f$), 8.51 (s, 1H, $J$ = 5.5 Hz, H$_i$), 8.37 (d, 1H, $J$ = 8.0 Hz, H$_j$), 7.93 (dt, 1H, $J$ = 1.8, 7.7 Hz, H$_k$), 7.67 (dd, 1H, $J$ = 2.1, 4.0 Hz, H$_l$), 7.44 (dd, 1H, $J$ = 1, 4.8 Hz, H$_e$), 3.66 (t, 2H, $J$ = 6.6 Hz, CH$_2$-H$_a$), 2.40 (t, 2H, $J$ = 6.8 Hz, CH$_2$-H$_d$).  

$^{13}$C NMR (DMSO-$d_6$) $\delta$ (ppm): 172.3, 156.1, 155.2, 150.1 (2C), 149.2, 148.6, 146.8, 137.2, 124.2, 120.4, 113.2, 109.8, 40.2, 36.1, 26.9, 21.9. MS-FAB m/z: calculated for C$_{18}$H$_{18}$N$_6$O$_4$ [M+H]$^+$: 383.1, found: 383.2.

$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (101 MHz, DMSO-d$_6$)

(Bipyridine)-(bipyridine-N-((2,2'-bipyridin)-4-yl)-5-(2,4,6-trioxo-1,3,5-triazinan-1-yl)
pentanamide) ruthenium hexafluorophosphate (4), [Ru(bpy)₂Cl₂] (54 mg, 0.11 mmol) was reacted with silver nitrate (37 mg, 0.22 mmol) in CH₂OH (5.4 mL) for 3 hours at room temperature under an Ar atmosphere. The suspension was filtered in order to remove the silver salt, and the filtrate was added to compound 3 (47 mg, 0.12 mmol). The solution was heated at reflux in the dark overnight under an Ar atmosphere. The reaction mixture was allowed to reach room temperature and the solvent was evaporated. The remaining solid was re-dissolved in a minimum amount of CH₂OH, and the desired compound was precipitated by dropwise addition of a saturated aqueous solution of ammonium hexafluorophosphate. The precipitate was filtered, washed with water and Et₂O and dried under vacuum to yield 4 as an orange solid; 100 mg, 85%. 

\[ \text{H NMR (CD₃CN)} \delta (ppm): 8.95 \text{ (br s, 1H), 8.83 \text{ (br s, 1H), 8.81 \text{ (d, 2H, } J = 2.0 \text{ Hz, Ar-H), 8.47 \text{ (d, 4H, } J = 8.2 \text{ Hz, Ar-H), 8.36 \text{ (d, 1H, } J = 6.7 \text{ Hz, Ar-H), 8.03 \text{ (m, 4H, Ar-H), 7.79 \text{ (d, 1H, } J = 5.6 \text{ Hz, Ar-H), 7.71 \text{ (m, 3H, Ar-H), 7.41 \text{ (m, 6H, Ar-H), 3.74 \text{ (t, 2H, } J = 5.3 \text{ Hz, CH₂), 2.45 \text{ (t, 2H, } J = 6.8 \text{ Hz, CH₂), 1.65 \text{ (m, 4H, 2CH₂). C NMR (CD₃CN)} \delta (ppm): 174.1, 158.3, 158.2 \text{ (2C), 158.1 \text{ (2C), 158.0, 152.8, 152.8, 152.7, 152.7 \text{ (2C), 152.6, 152.6, 150.6 \text{ (2C), 148.8, 148.5, 138.8, 138.6 \text{ (3C), 128.6, 128.5, 128.5 \text{ (3C), 125.2, 125.2 \text{ (2C), 125.1, 118.3, 117.4, 114.7, 41.7, 37.3, 27.9, 22.7 ppm. MS-MALDI-TOF m/z: calculated for C₃₈H₃₄F₆N₁₀O₄PRu [M+PF₆]⁺: 941.1, found: 941.2; calculated for C₃₈H₃₄N₁₀O₄Ru [M]: 795.2, found: 795.2.} }\]
$^1$C NMR (101 MHz, CD$_3$CN)

MeOH

n-hexane
b) HR synthesis

The 5-amino-\(N,N'\)-bis[6-(3,3-dimethylbutyrylamo) pyridin-2-yl] isophthalamide, compound 8, was synthesized as described by Dirksen et al.\(^1\) The experimental procedures followed are explained below.

\[\text{N-(6-Aminopyridin-2-yl)-3,3-dimethylbutyramide (5). A solution of 3,3-dimethylbutyryl chloride (3 g, 22.3 mmol) in dry THF (12 mL) was added to a solution of 2,6-diaminopyridine (2.43 g, 22.3 mmol) and triethylamine (3.1 mL, 22.3 mmol) in dry THF (25 mL) at 0°C under an argon atmosphere over a period of 2 h. The solution was stirred for 60 h at room temperature, the residue filtered off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (DCM/ethyl acetate 4:1 as eluent) gave 5 as a colorless solid; 2.9 g, 63%.} \]

\[\text{\(1H\) NMR (CDCl\textsubscript{3}) \(\delta\) (ppm): 7.77 (br s, 1H, CONH), 7.55 (d, 1H, \(J = \))}\]
7.9 Hz, Hpy), 7.42 (t, 1H, J = 8.0 Hz; Hpy), 6.22 (d, 1H, J = 7.9 Hz, Hpy), 4.34 (br s, 2H; NH), 2.17 (s, 2H; (CH₂C(CH₃)₃), 1.05 (s, 9H; (C(CH₃)₃).

1H NMR (400 MHz, CDCl₃)

5-Nitroisophthaloyl dichloride (6). A solution of 5-nitroisophthalic acid (3.0 g, 14.0 mmol) in thionyl chloride (5 mL) and N,N’-dimethylformamide (five drops) was refluxed for 6 h under dry conditions with subsequent vacuum distillation of the thionyl chloride excess. The residue was dried under high vacuum and yielded 6 as a white solid; 2.6 g, 98%; 1H NMR (DMSO-d₆) δ (ppm): 8.77 (d, J = 1.52 Hz, 2H; Ar-H), 8.74 (t, J = 1.52 Hz, 1H; Ar-H).
**H NMR (400 MHz, DMSO-d<sub>6</sub>)

N,N'-Bis[6-(3,3-dimethylbutrylamino)pyridin-2-yl]-5-nitro-isophthalamide (7). A solution of diacid dichloride 6 (0.9 g, 3.62 mmol) in dry THF (15 mL) was added dropwise to a solution of monosubstituted diaminopyridine 5 (1.5 g, 7.24 mmol) and triethylamine (1 mL, 7.24 mmol) in dry THF (15 mL) at 0 °C under an argon atmosphere. The mixture was stirred at r.t. for 12 h. After this time, the residue was filtered off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (DCM/ethyl acetate 10:1-3:1 as eluent) gave 7 as a yellowish solid; 2.1 g, 98%: H NMR (CDCl<sub>3</sub>) δ (ppm): 8.91 (br d, J = 1.3 Hz, 2H; CONH), 8.80 (br t, J = 1.3 Hz, 1H; Ar-H), 8.46 (br s, 2H; Ar-H), 8.02 (t, J = 8.0 Hz, 4H; Hpy), 7.79 (t, J = 8.0 Hz, 2H; Hpy), 7.66 (br s, 2H; CONH), 2.28 (s, 4H; COCH<sub>3</sub>), 1.13 (s, 18H; C(CH<sub>3</sub>)).
5-Amino-N,N'-bis[6-(3,3-dimethylbutyrylamo)pyridin-2-yl]isophthalamide  (8).

To a solution of 7 (0.4 g, 0.68 mmol) in dry THF (34 mL) and MeOH (34 mL) under argon atmosphere, 10% Pd-C (400 mg) was added and the reaction mixture was heated to 70 ºC. Then hydrazine (1.1 mL, 20.4 mmol) was added to the reaction mixture, which was heated under reflux for 4h. Once the reaction was completed (TLC). The catalyst was filtered off over celite and the solvent removed under reduced pressure to give a yellowish solid (0.3 g, 79%). 1H NMR (CDCl₃) δ (ppm): 8.47 (s, 2H; CONH), 8.10 (s, 2H; CONH), 7.93 (br t, 4H; Hpy), 7.66 (m, 3H; 2H-py, Ar-H), 4.08 (br s, 2H, NH₂), 2.26 (s, 4H; 2CH₂), 1.11 (s, 18H; C(CH₃)₃).
5-benzamido-\(N,N\)\(^-\)bis(6-(3,3-dimethylbutyrylamino)pyridin-2-yl)isophthalamide (9).

A solution of benzoyl chloride (21 mg, 0.15 mmol) in dry THF (1 mL) was added dropwise to a solution of 8 (50 mg, 0.09 mmol) and triethylamine (16 L, 0.12 mmol) in dry THF (2 mL) at 0 °C under an argon atmosphere. The mixture was stirred at r.t. for 12 h, the residue filtered off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (DCM/MeOH 15:1 as eluent) gave 9 as a yellowish oil; 40 mg, 68%. \(\text{H NMR (CDCl}_3\) \(\delta\) (ppm): 9.24 (br s, 1H), 8.97 (br s, 2H), 8.48 (br s, 2H), 7.99 (m, 3H), 7.90 (d, 2H, \(J = 8.0\) Hz), 7.76 (d, 2H, \(J = 7.8\) Hz), 7.53 (m, 3H), 7.41 (t, 2H, \(J = 7.5\) Hz), 2.42 (s, 4H), 1.23 (s, 18H); \(\text{C NMR (CDCl}_3\) \(\delta\) (ppm): 171.7 (2C), 170.1, 167.0, 163.9, 150.1 (2C), 148.8 (2C), 140.6 (2C), 139.2, 135.0, 133.6, 132.6 (2C), 130.1, 128.8 (2C), 128.3, 127.5 (2C), 122.2, 122.0, 110.6 (2C), 109.4 (2C), 50.9 (2C), 31.5 (2C), 29.8 (6C).
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
S3. Synthesis of the Ammonium derivative (Am)

Boc-H-COO + \( \text{Ar-NH}_2 \) \( \xrightarrow{\text{EDC, DMAP}} \) \( \text{Boc-NH} - \text{Ar-NH}_2 \) \( \xrightarrow{\text{CH}_2\text{Cl}_2, 0^\circ \text{C to r.t.}} \) 10 (75%)

Boc-NH-CO-NH- \( \text{Ar} \) \( \xrightarrow{\text{TFA}} \) \( \text{Boc-NH-CO-NH-} \text{Ar} \) \( \xrightarrow{\text{DCM, 0^\circ C to r.t.}} \) 11 (99%)

\( \text{Ru-N} - \text{Ar-N} + \text{H}_3\text{N}-\text{CO-} \) \( \xrightarrow{\text{CF}_3\text{COO}^-} \) \( \text{Ru-N} - \text{Ar-N} + \text{CF}_3\text{COO}^- \) \( \xrightarrow{\text{Ar, r.t. to reflux}} \) \( \text{Ru-N} - \text{Ar-N} + \text{CF}_3\text{COO}^- \) \( \xrightarrow{\text{i) AgNO}_3, \text{MeOH, reflux}} \) \( \text{Ru-N} - \text{Ar-N} + \text{CF}_3\text{COO}^- \) \( \xrightarrow{\text{ii) NH}_4\text{PF}_6} \) 12 (84%)
tert-butyl (3-([2,2'-bipyridin]-4-ylamino)-3-oxopropyl)carbamate (10). 3-((tert-butoxycarbonyl) amino)propanoic acid (133 mg, 0.70 mmol) was dissolved in CHCl₃ (6 mL) and the solution was cooled to 0 °C. EDCI·HCl (168 mg, 0.88 mmol) and DMAP (122 mg, 0.99 mmol) were added. The reaction mixture was allowed to stir at room temperature for 30 minutes. A solution of [2,2'-bipyridin]-4-amine (100 mg, 0.58 mmol) in CHCl₃ (4 mL) was added to the activated acid. The reaction mixture was stirred overnight, concentrated under reduced pressure and the crude material was purified by column chromatography (eluent: DCM/MeOH 50:1-40:1) to give 10 as colorless oil; 150 mg, 75%. ¹H NMR (CDCl₃) δ (ppm): 8.70 (s, 1H, NH), 8.63 (d, 1H, J = 4.8 Hz, H), 8.53 (d, 1H, J = 5.5 Hz, H), 8.40 (br s, 1H, H), 8.33 (d, 1H, J = 8.0 Hz, H), 7.78 (dt, 1H, J = 1.8, 7.7 Hz, H), 7.63 (m, 1H, H), 7.28 (ddd, 1H, J = 0.8, 4.8, 7.5 Hz, H), 5.33 (br s, 1H, NH), 3.48 (q, 2H, J = 6.2 Hz, CH₂-H), 2.64 (t, 2H, J = 7.0 Hz, CH₂-H); 1.42 (s, 9H, 3CH₃-Boc). ¹³C NMR δ (ppm): 170.7, 157.1, 156.4, 155.7, 150.2, 149.1, 146.0, 136.9, 123.9, 121.1, 113.7, 110.9, 79.8, 37.8, 36.3, 28.4.

¹H NMR (400 MHz, CDCl₃)
3-([2,2′-bipyridin]-4-ylamino)-3-oxopropan-1-aminium 2,2,2-trifluoroacetate (11).

To a solution of 10 (60 mg, 0.18 mmol) in DCM (1.5 mL) was added TFA (0.1 mL) at 0 °C. The reaction was stirred at room temperature for 3 h until it was completed (TLC). The reaction mixture was concentrated under reduced pressure and DCM was added. The organic layer was washed twice with brine, dried over Na₂SO₄, concentrated under reduced pressure and dried under high vacuum to give compound 11 as a yellowish oil; quantitative yield. The crude material was used directly in the next step reaction.

(Bipyridine)-(bipyridine-N-([2,2′-bipyridin]-4-yl)-5-(2,4,6-trioxo-1,3,5-triazinan-1-yl) pentanamide) ruthenium hexafluorophosphate (12, Am). [Ru(bpy)₂Cl₂] (54 mg, 0.11 mmol) was reacted with silver nitrate (37 mg, 0.22 mmol) in CH₃OH (5.4 mL) for 3 h at room temperature under an argon atmosphere. The suspension was filtered in order to remove the silver salt, and the filtrate was added to 11 (44 mg, 0.12 mmol). The solution was stirred at room temperature in the dark overnight under an argon atmosphere. The solvent was evaporated. The remaining solid was re-dissolved in a minimum amount of CH₃OH, and the desired compound was precipitated by dropwise addition of a saturated aqueous solution of ammonium.
hexafluorophosphate. The precipitate was filtered, washed with water and EtO and dried under vacuum. 12 was obtained as a brown solid; 97 mg, 84%. H NMR (CD$_3$CN) δ (ppm): 9.25 (br s, 1H, NH), 8.64 (br s, 1H), 8.49 (d, 4H, J = 8.2 Hz, Ar-H), 8.35 (d, 1H, J = 7.8 Hz, Ar-H), 8.04 (m, 4H, Ar-H), 7.80 (d, 1H, J = 5.6 Hz, Ar-H), 7.72 (m, 4H, Ar-H), 7.53 (s, 2H), 7.38 (m, 5H, Ar-H), 6.37 (br s, 3H, NH), 3.27 (t, 2H, J = 6.2 Hz, CH$_2$), 2.83 (t, 2H, J = 6.2 Hz, CH$_2$). 13C NMR (CD$_3$CN) δ (ppm): 172.0, 158.5, 158.0, 157.8, 153.0, 152.8, 152.7, 152.7, 149.3, 147.5, 145.8, 145.6, 145.2, 144.7, 138.9, 138.7 (2C), 131.1, 131.0, 130.7, 130.4, 128.7, 128.5 (2C), 127.4, 126.9, 125.2 (2C), 125.1, 117.6, 114.3, 37.1, 33.3. MS-ESI m/z: calculated for C$_{33}$H$_{31}$F$_6$N$_8$OPRu [M+PF$_6$]: 801.7, found: 801.1.

**H NMR (400 MHz, CD$_3$CN)**

![NMR spectrum image]
13C NMR (101 MHz, CD$_3$CN)
**S4. SWNTs functionalization**

A mixture of SWNTs (1 mg·mL⁻¹) in NMP (10 mL) was ultrasonicated for 20 min. After this time, the correspondent host molecule (the aniline derivatized Hamilton receptor or the 4'-Aminobenzo-18-crown-6) (3.3 mg/mg SWNT, 0.1 equiv.) and boron trifluoride diethyl etherate (0.2 equiv.) were added. The suspension was stirred for 15 min and isoamyl nitrite (0.1 equiv.) was added. The mixture was stirred for 5 h and the SWNTs were filtered through a 0.2 μm-pore PTFE membrane. The final hybrids were washed several times with THF to ensure the total removal of adsorbed host molecules.

**Figure 1.** a) TGA analysis (Air, 10⁰C·min⁻¹) of pristine SWNT (black) and 18-crown-6 functionalized SWNTs (SWNT-crown) (green), functionalization corresponds to a total 14% weight (the first weight loss corresponds to solvent impurities and has not been considered). b) TGA analysis (Air, 10⁰C·min⁻¹) of pristine SWNT (black) and Hamilton receptor functionalized SWNTs (SWNT-HR) (blue), functionalization corresponds to a total 20% weight.

**S5. Procedure for the UV/Vis titration experiments**

Absolute concentrations for each component of the titration experiment were determined by standard calibration curves. The appropriate aliquots were added relative to the determined concentrations. All titration were performed with a background concentration of host in the guest solution so as to maintain a constant concentration of host species. Aliquot injections were carried out with MICROMAN™ E positive displacement pipettes into a quartz cuvette (cuvette path length was dependent on concentrations used: 1.0 mm or 10.0 mm). The cuvettes were closed with a Teflon stopper.

Each spectrum was acquired at a resolution of 1.0 nm and an integration time of 0.1 s. Spectral analyses were performed using the ReactLab™ Equilibria spectral analyses suite (JplusConsulting, www.jplusconsulting.com). Repetitions of the binding experiments for each complex gave association constants within 10% of the values shown below (the error in data fitting for each experiment was <5%).
a) Example of UV/Vis titration experiment for the HR vs Cy couple

**Figure 2:** UV/Vis spectra of 4 (ca. 4·10⁻⁶ M) upon addition of 9 (0 → 2 equiv.), while maintaining the concentration of 4 constant, in CHCN at 298 K.

**Figure 3:** UV/Vis titration of 4 with 9 in CHCN, ReactLab Working Window. Top left, plot of least-squares optimization during a fit. Top right, a 3D plot of the residuals for the fit. Bottom left, the calculated spectrum for each species. Bottom right, concentration profile for the species in solution.
Figure 4: UV/Vis titration of 4 with 9 in CH3CN, ReactLab Input/Output spreadsheet displaying log $K_a = 6.233$.

b) Example of UV/Vis titration experiment for the 18-Crown-6 vs Am couple.

Figure 5: UV/Vis spectra of 12 (ca. 2.6·10$^{-4}$ M) upon addition of 18-Crown-6 (0 → 2 equiv.), while maintaining the concentration of 9 constant, in CH3CN at 298 K.
Figure 6: UV/Vis titration of 12 with 18-Crown-6 in CH3CN, ReactLab Working Window. Top left, plot of least-squares optimization during a fit. Top right, a 3D plot of the residuals for the fit. Bottom left, the calculated spectrum for each species. Bottom right, concentration profile for the species in solution.
**Figure 7:** UV/Vis titration of 12 with 18-Crown-6 in CH₃CN, ReactLab Input/Output spreadsheet displaying log $K_a = 3.756$.

**S6. TGA titration experiments procedure**

The titration curve for each host is obtained using the TGA results of independent incubation experiments performed with different guest concentration. Each experiment proceeds as follows: the guest molecule is dissolved in acetonitrile (due to solubility). Functionalized SWNTs are added (1 mg·mL⁻¹) and the suspension is stirred for 2 h at room temperature. Then, the mixture is filtered through a 0.2 µm-pore PTFE membrane. The solid obtained is dried under vacuum and characterized by TGA (Air, 10 °C·min⁻¹). The weight loss is measured in the range 250 °C - 450 °C. Each independent experiment for each guest concentration is repeated 3 times and the different results are averaged. A blank to determine the solvent adsorbed on or encapsulated in the SWNTs is carried out. The value of solvent encapsulated/adsorbed is subtracted from the final data.
a) Thermogravimetric plots

**Figure 8.** TGA analysis of the titration of the Ruthenium dye-derivated cyanuric acid (Cy) vs SWNT-HR in acetonitrile at 1 mg·mL⁻¹ of SWNTs-HR.

**Figure 9.** TGA analysis of the titration of the Ruthenium dye-derivated ammonium (Am) vs SWNT-Crown in acetonitrile at 1 mg·mL⁻¹ of SWNTs-Crown.
S7. References

[1] A. Dirksen, U. Hahn, F. Schwanke, M. Nieger, J. N. H. Reek, F. Vögtle, L. De Cola, *Chem. Eur. J.* 2004, 10, 2036-2047.

[2] R. Gatri, I. Ouerfelli, M. L. Efrit, F. Serein-Spirau, J.-P. Lère-Porte, P. Valvin, T. Roisnel, S. Bivaud, H. Akdas-Kilig, J.-L. Fillaut, *Organometallics* 2014, 33, 665-676.

[3] C.-H. Huang, N. D. McClenaghan, A. Kuhn, G. Bravic, D. M. Bassani, *Tetrahedron* 2006, 62, 2050-2059.

[4] X. Liu, Y. Wang, C. Chen, A. Tintaru, Y. Cao, J. Liu, F. Ziarelli, J. Tang, H. Guo, R. Rosas, S. Giorgio, L. Charles, P. Rocchi, L. Peng, *Adv. Funct. Mater.* 2016, 26, 8594-8603.

[5] J. E. Sader, J. W. M. Chon, P. Mulvaney, *Rev. Sci. Instrum.* 1999, 70, 3967-3969.