Electronic Supplementary Information (ESI) for:

Hydrogen-bonded metallo-supramolecular polymers based on ruthenium or iron complexes for the selective extraction of single-walled carbon nanotubes

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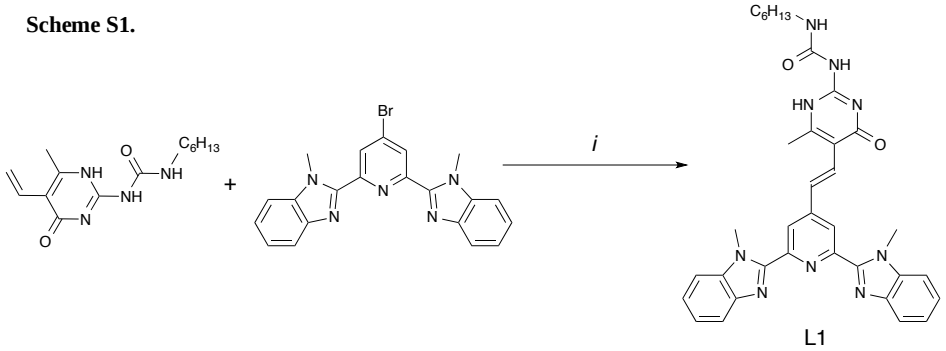
1. Synthesis of Ru compounds that do not contain long alkyl chains.

1-1: Preparation of Ligand L1, which contains the H-bonding moiety

Scheme S1.

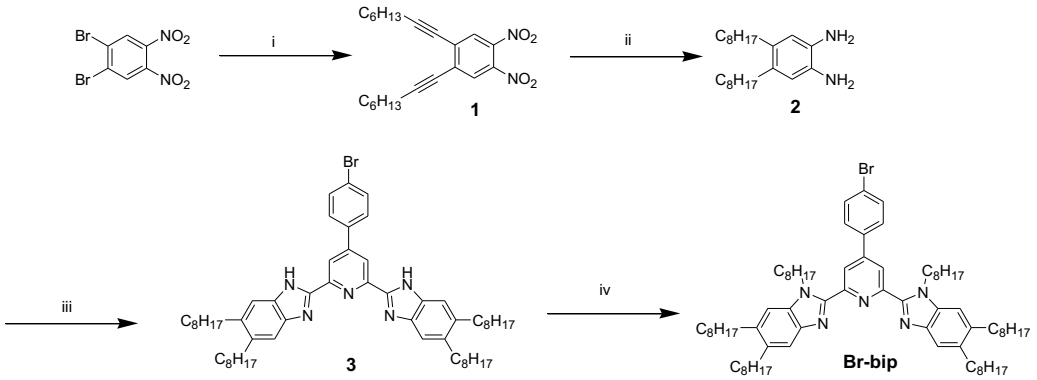


Reaction conditions: (*i*) $Pd(OAc)_2$, P(*o*-tolyl)$_3$ in DMF.

4-Bromo-2,6-bis(N-methylbenzimidazol-2-yl)pyridine (1.02 g, 2.44 mmol), 1-hexyl-3-(6-methyl-5-ethenyl-4-oxo-1,4-dihydro-2-pyrimidinyl)urea (0.863 g, 3.10 mmol), palladium(II) acetate (58.1 mg, 0.26 mmol) and tri(*o*-tolyl)phosphine (154.0 mg, 0.506 mmol) were dissolved in dry DMF (115 mL) and trimethylamine (35 mL) was added under an atmosphere of N_2. The mixture was stirred at 95 °C for 21 h. After cooling to room temperature, the reaction mixture was filtered, and all volatiles were evaporated from the filtrate *in vacuo*. Upon addition of ethanol, an orange precipitate was obtained, which was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 98/2, v/v) to give the targeted product as a yellow solid (0.34 g, 23%).^{1}H NMR (DMSO-d_6,500 MHz): δ (ppm) 8.46 (s, 2H), 7.96 (d, *J* = 15.5 Hz, 1H), 7.79 (t, *J* = 9.9 Hz, 4H), 7.56 (d, *J* = 15.8 Hz, 1H), 7.41 (dt, *J* = 25.6, 7.3 Hz, 4H), 4.29 (s, 6H), 3.15 (s, 2H), 1.44 (s, 2H), 1.26 (s, 6H), 0.85 (t, *J* = 6.3 Hz, 3H).

2. Synthesis of ligand precursors with a long-chain alkylated 2,6-bis(benzimidazol-2-yl)pyridine moiety

Scheme S2.



Reaction conditions: (i) 1-octyne, $Pd(PPh_3)_4$, CuI, TE in THF; (ii) hydrazine monohydrate, Pd/C in EtOH; (iii) bdde in PPA; (iv) $C_8H_{17}Br$, K_2CO_3 in dry DMF.

2-1. 4,5-Di(octyn-1-yl)-1,2-dinitrobenzene (1). A mixture of 1,2-dibromo-4,5-dinitrobenzene (7.42 g, 22.8 mmol), cuprous iodide (0.43 g, 2.25 mmol), and tetrakis(triphenylphosphine)palladium (1.25 mg, 1.08 mmol) was dissolved in THF (280 mL) under an atmosphere of N_2, before triethylamine (15 mL) and 1-octyne (7 mL, 47.6 mmol) were added. The reaction mixture was stirred at room temperature for 90 h. The solution was filtered, and the filtrate concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent: hexane) to give **1** as a yellow oil (6.14 g, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.85 (s, 2H), 2.50 (t, *J* = 7.1 Hz, 4H), 1.67-1.62 (m, 4H), 1.50-1.44 (m, 4H), 1.38-1.27 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 6H).

2-2. 1,2-Diamino-4,5-dioctylbenzene (2). A three-necked round-bottomed flask (100 mL) was charged with 10% Pd/C (300 mg) and flushed with nitrogen, before a solution of **1** (1.21 mg, 3.15 mmol) in ethanol (30 mL) and hydrazine monohydrate (21 mL) were added via syringe. The resulting mixture was heated to reflux for 15 h. After cooling to room temperature, the solution was filtered, and the filtrate was concentrated under reduced pressure. Purification of the thus obtained residue was achieved by column chromatography on silica gel (eluent: ethyl acetate/hexane = 1/1, v/v) to give **2** as yellow oil (0.76 g, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.50 (s, 2H), 2.44 (t, *J* = 7.9 Hz, 4H), 1.53-1.48 (m, 4H), 1.30-1.23 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 6H).

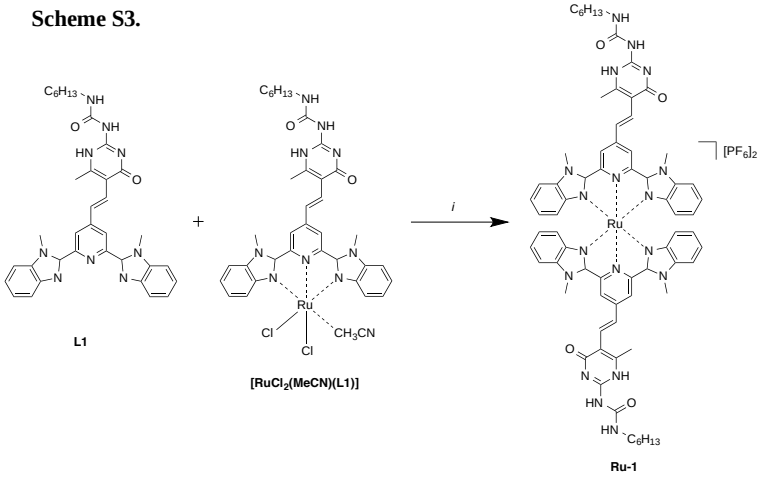
2-3. 4-(4-Bromophenyl)-2,6-bis(6,7-dioctylbenzimidazol-2-yl)pyridine (3). A mixture of 4-(4-bromophenyl)-2,6-dipicolinic acid dimethyl ester (bdde) (0.40 g, 1.15 mmol), 1,2-diamino-4,5-dioctylbenzene (**2**) (0.76 g, 2.29 mmol) and polyphosphoric acid (5 mL) was stirred at 170 °C for

14 h. The reaction mixture was poured into 100 mL of distilled water and the pH was adjusted to 11 by addition of ammonium hydroxide. The thus obtained precipitate was isolated by filtration and washed with distilled water. This crude product was used in the subsequent step without further purification (0.62 g, 59%). MALDI-TOF-MS: *m*/*z* = 916.8893 $[M+H]^+$ (calcd for $C_{57}H_{81}BrN_5$, 917.5781).

2-4. 4-(4-Bromophenyl)-2,6-bis(1,6,7-trioctylbenzimidazol-2-yl)pyridine (Br-bip). 4-(4-bromophenyl)-2,6-bis(6,7-dioctylbenzimidazol- 2-yl)pyridine **(3)** (0.62 g, 0.68 mmol), 1-bromooctane (0.38 g, 1.97 mmol), and potassium carbonate (0.34 g, 2.47 mmol) were dissolved in DMF (3 mL). The reaction mixture was stirred at room temperature for 17 h. The mixture was concentrated under reduced pressure, before the thus obtained residue was dissolved in CH_2Cl_2 (20 mL) and filtered. After the filtrate was washed with water (2 × 20 mL) and brine (20 mL), the organic phase was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/hexane = 1/1, v/v) to afford **4** as a light brown oil (0.76 g, 97%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.49 (d, *J* = 0.7 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 3.9Hz, 4H), 7.20 (s, 2H), 4.70 (t, *J* = 7.4 Hz, 4H), 2.76 (dd, *J* = 16.0, 10.7 Hz, 12H), 1.72-1.66 (m, 17H), 1.44-1.23 (m, 71H), 1.10-1.01 (m, 28H), 0.91-0.87 (m, 28H), 0.74 (t, *J* = 7.2 Hz, 7H).

3. Synthesis of Ru-1

Scheme S3.



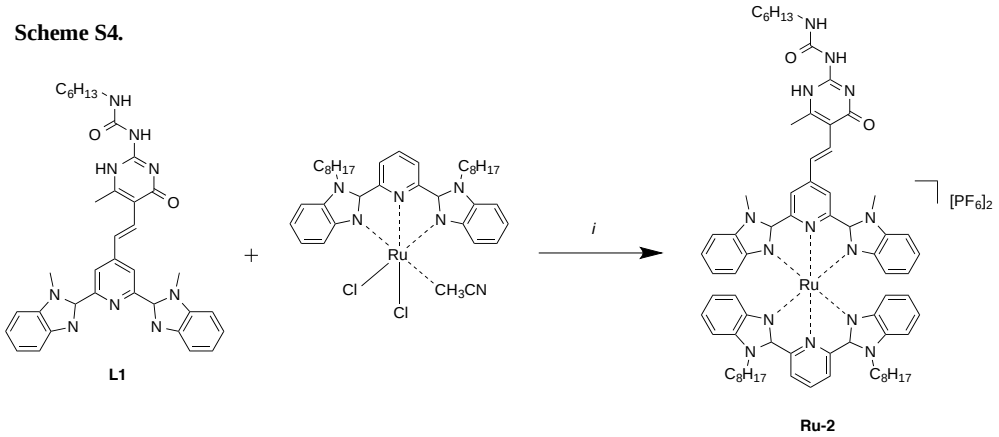
Reaction condition: *(i)* 1.) ethylene glycol, 120 °C, 6 h; 2.) $K[PF_6]$.

Dichloroido(*p*-cymene)ruthenium(II) dimer (49.8 mg, 81.4 μmol) and **L1** (101 mg, 163 μmol) were dissolved in dry acetonitrile (10 mL) under an atmosphere of N_2. The resulting mixture was heated to 80 °C for 4 h. After the removal of all the volatiles under reduced pressure, [$RuCl_2$(MeCN)(**L1**)] was obtained as a red solid (84.4 mg, 61%). This solid was used for the subsequent reaction without further purification.

[$RuCl_2$(MeCN)(**L1**)] (77.35 mg, 93.3 μmol) and **L1** (57.72 mg, 93.7 μmol) were dissolved in ethylene glycol (15 mL) under an atmosphere of N_2. The solution was stirred at 120 °C for 6 h, before a saturated aqueous solution of K[PF_6] (10 mL) was added and the resulting precipitate was isolated by filtration. The crude product was purified by Sephadex LH-20 chromatography (eluent: MeOH/MeCN = 1/1, v/v) to obtain pure **Ru-1** as a violet solid (56.4 mg, 37%).

4. Synthesis of Ru-2

Scheme S4.



Reaction condition: (*i*) heated in ethylene glycol, and then KPF_6

A mixture of [$RuCl_2$(MeCN)(bip-octyl)] (60.1 mg, 0.080 mmol) and **L1** (49.4 mg, 0.081 mmol) in ethylene glycol (15 mL) was stirred at 100 °C for 3 h under an atmosphere of N_2, which resulted in a color change to red-violet. After cooling to room temperature, water (10 mL) was added to the resulting solution, and then an aqueous solution of K[PF_6], which afforded a red-violet precipitate. The precipitate was collected by filtration and purified by column chromatography (Sephadex LH-20; eluent: methanol/acetonitrile = 1/1, v,v) to obtain **Ru-2** as a red solid (17.7 mg, 14%).

^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 8.92 (s, 2H), 8.78 (d, *J* = 8.3 Hz, 2H), 8.73 (d, J = 14.9 Hz, 1H), 8.57 (t, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 16.3 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 4H), 7.47 (d, *J* = 8.3 Hz, 4H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.26 (t, *J* = 7.6 Hz, 4H), 6.32 (d, *J* = 8.0 Hz, 2H), 6.05 (d, *J* = 8.0 Hz, 2H), 4.82 (t, *J* = 6.6 Hz, 4H), 4.45 (s, 6H), 3.28 (s, 2H), 2.72 (s, 3H), 1.63 (s, 2H), 1.37 (s, 8H), 1.08 (s, 13H), 0.93 (s, 12H), 0.76 (t, *J* = 7.2 Hz, 3H).

5. Spectral data for UPy-bip and Ru-2.

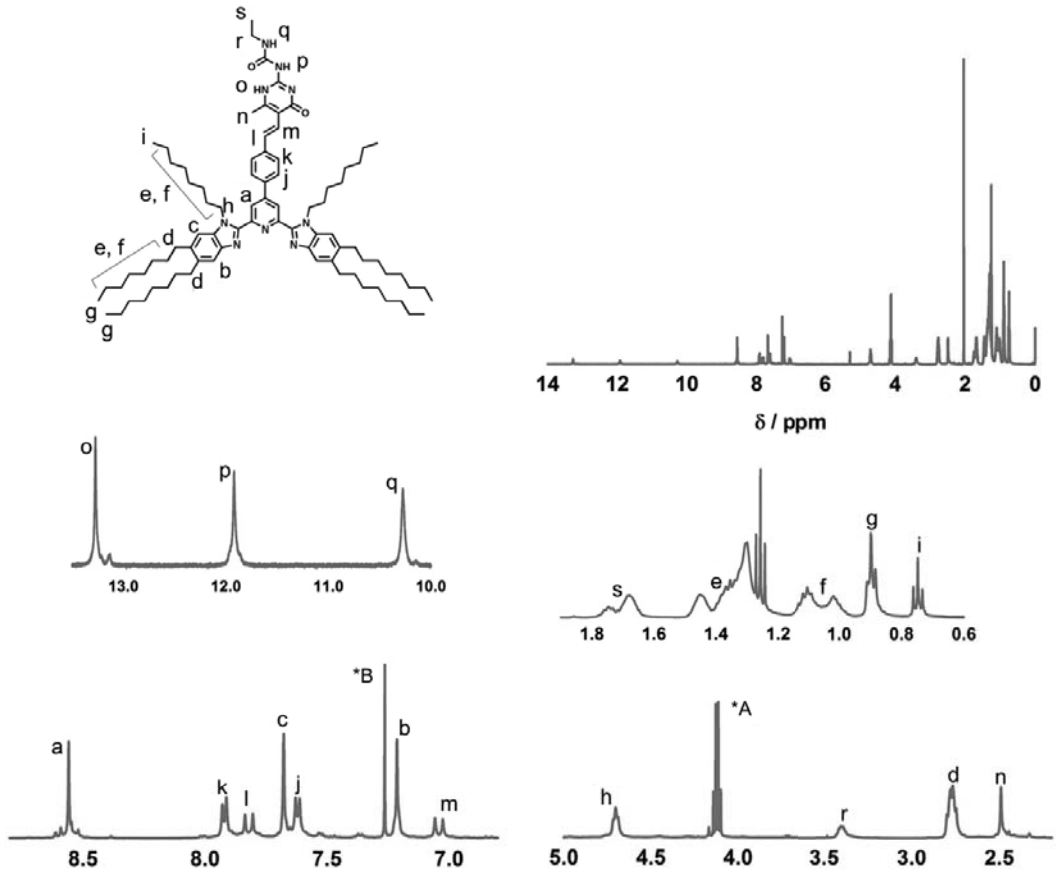


Fig. S1. ^{1}H NMR spectra of **UPy-bip** in $CDCl_3$ (500 MHz).

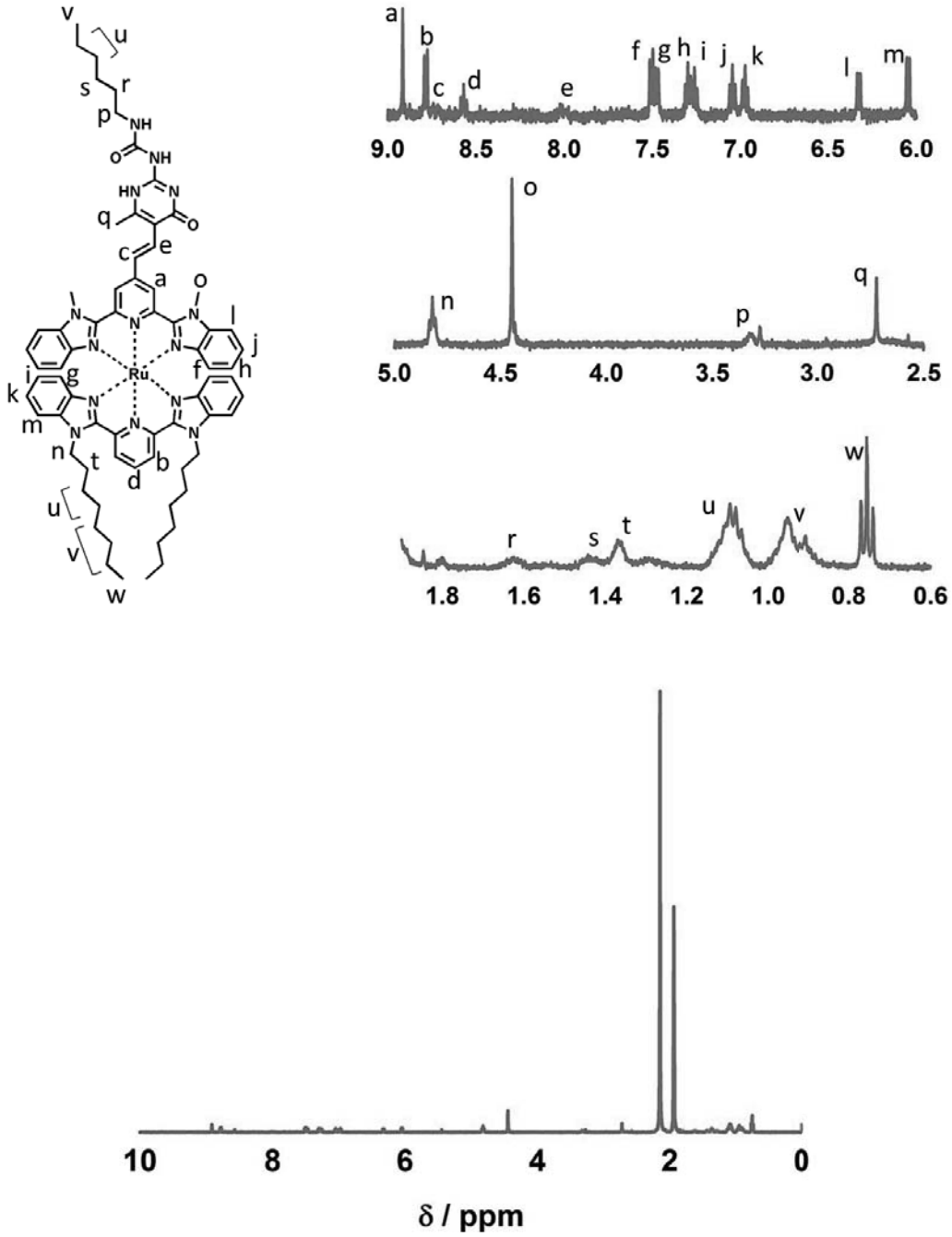


Fig. S2. ^{1}H NMR spectra of **Ru-2** in $CDCl_3$ (500 MHz).

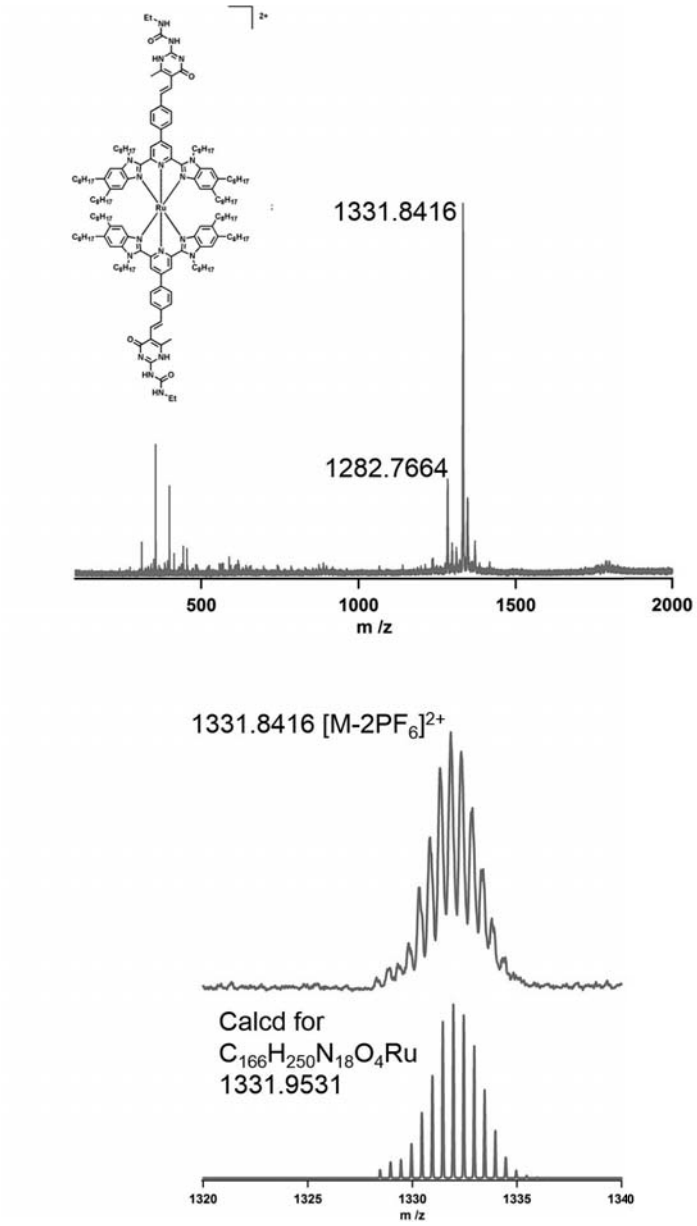


Fig. S3. ESI-MS spectra of **Ru-UPy** in CH_3CN.

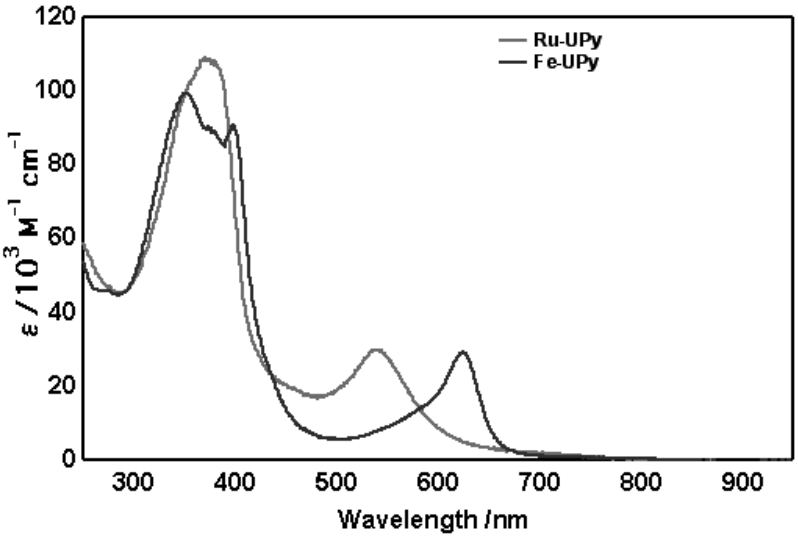


Fig. S4 UV-Vis spectra for **Ru-UPy** (red) and **Fe-UPy** (blue) in dichloromethane.

6. Determination of H-bonded self-association constants for the model complex Ru-2

The concentration dependence on the change of ^{1}H NMR chemical shift of the methyl groups on the UPy moieties in **Ru-2** is shown in Figure S1. Since only one methyl signal was observed in the concentration range for **Ru-2**, a fast exchange between monomer and dimer was assumed.

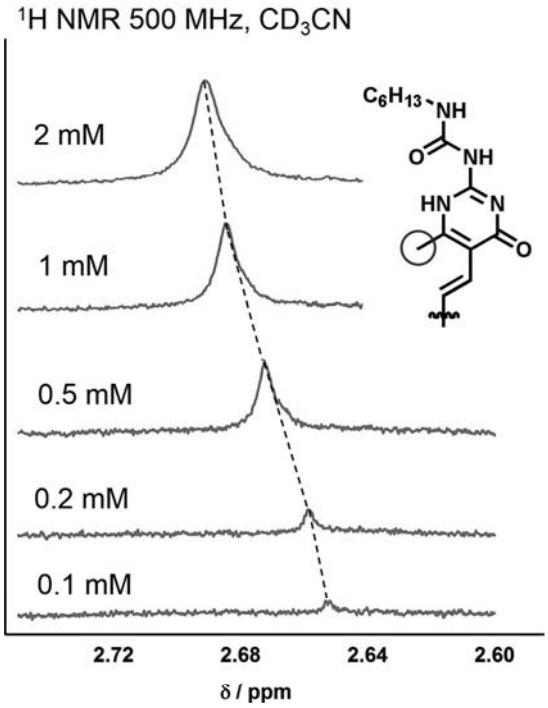
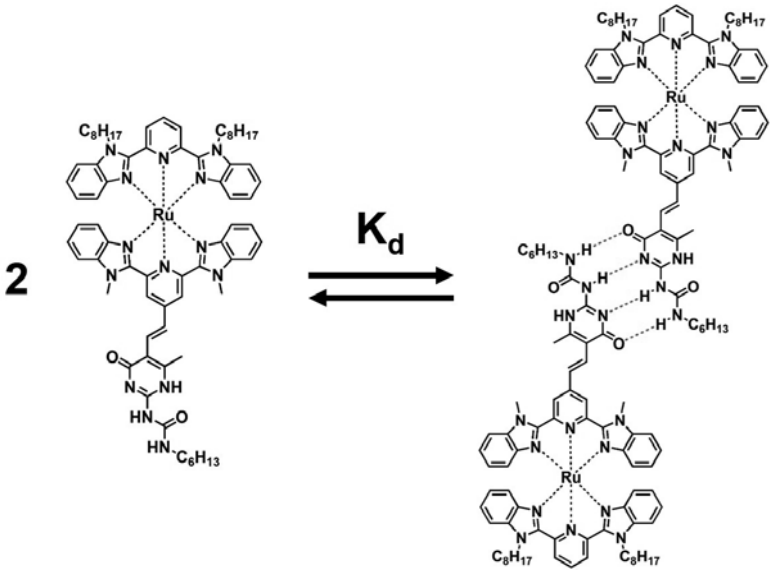


Fig S5. ^{1}H NMR spectral change for the methyl protons on the UPy moieties of **Ru-2** upon increasing the concentration of the Ru complex in CD_3CN.



Considering the dimerization, the observed chemical shift can be expressed by:

$$\delta_{obs} = x_m\delta_m + x_d\delta_d$$

where δ_m and δ_d refer to the chemical shifts, and χ_m and χ_d to the molar fractions of monomer and dimer, respectively.

$$x_m = \frac{[M]}{[M]+2[D]}$$

$$x_d = \frac{2[D]}{[M]+2[D]}$$

The observed chemical shift δ_{obs} can thus be expressed by:

$$\delta_{obs} = \delta_m\left(\frac{-1+\sqrt{8K_dC+1}}{4K_dC}\right) + \delta_d\left(\frac{4K_dC+1-\sqrt{8K_dC+1}}{4K_dC}\right)$$

wherein C and K_d refer to the initial concentration of the Ru complex and the equilibrium constant for the dimerization, respectively. Applying a non-linear data fitting for the plots of the chemical shift as a function of the concentration in Figure X afforded $K_d = (1.02\times10^3) \pm 355$ M^{-1}, $\delta_m = 2.64 \pm 0.004$ ppm, and $\delta_d = 2.73 \pm 0.006$ ppm.

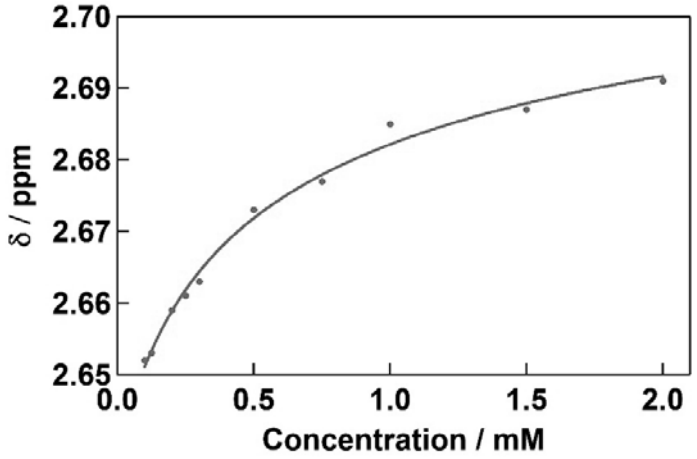


Fig S6 Plot of the ^{1}H NMR chemical shift for the **UPy** methyl protons as a function of the concentration of **Ru-2**: observed data points (red dots) and non-linear data fitting (red line).

7. DLS-derived size distribution of the particles

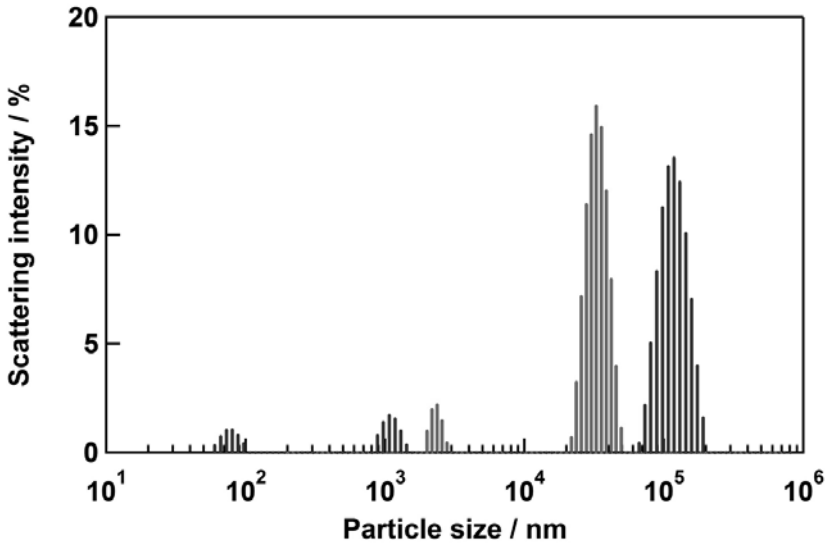


Fig S7. DLS-derived size distribution of the particles from two different concentrations of **Ru-UPy** in chlorobenzene: [Ru] = 0.1 mg (blue) and 1.5 mg (red) in 3 mL chlorobenzene.

8. CPK model of Ru-UPy on (6,5)-SWNT

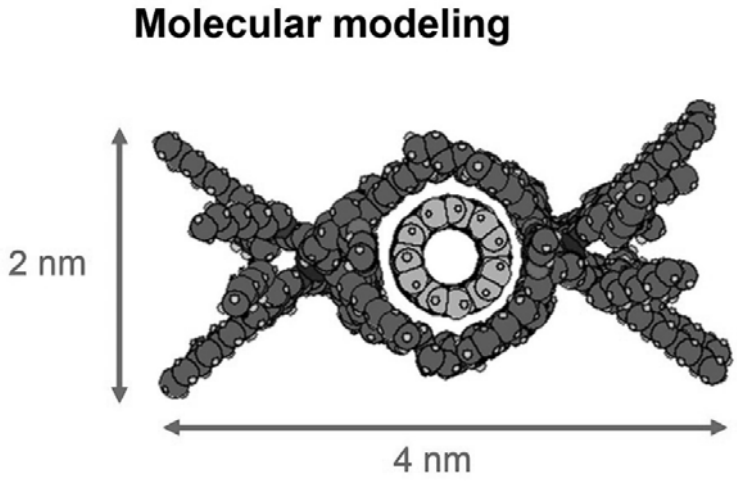


Fig. S8. CPK model of **Ru-UPy** on (6,5)-SWNT.

9. PL map for SWNT dissolved by SDS in water

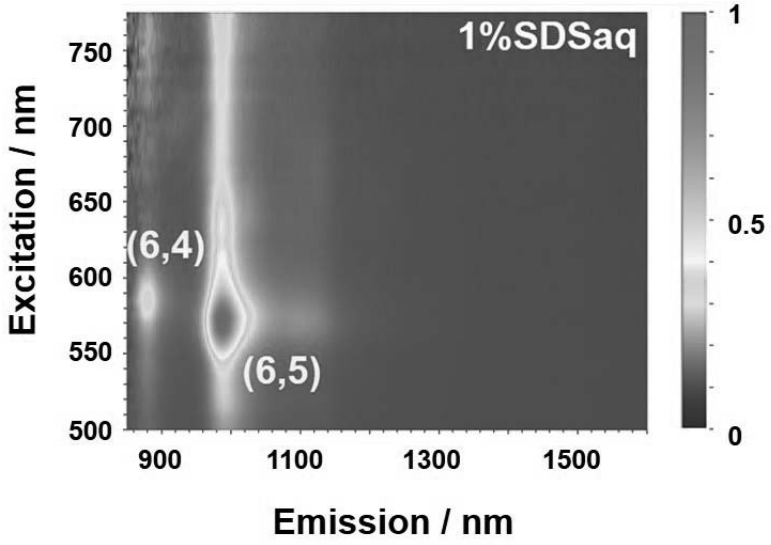


Fig. S9 PL map for SDS/SWNT in water (SDS: 1%).

10. G and D band regions in the Raman spectra of Ru-UPy, Fe-UPy/SWNT, and SDS/SWNT

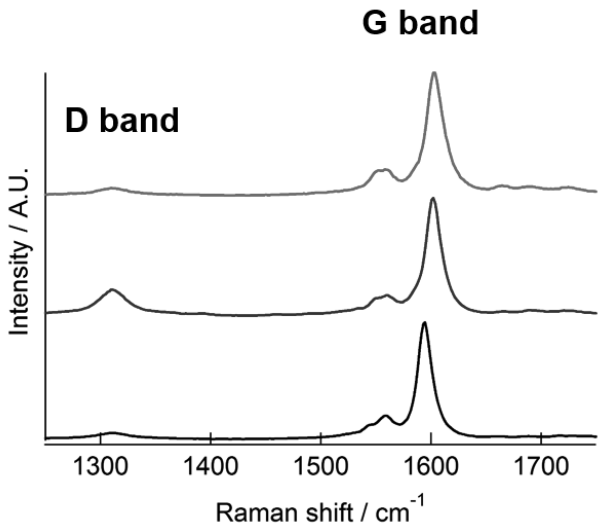


Fig. S10. G and D band regions in the Raman spectra of **Ru-UPy**/SWNT (red), **Fe-UPy**/SWNT (blue), and SDS/SWNT (black) on silicone substrates.

11. UV-vis-NIR spectrum for (6,5)-enriched SWNTs

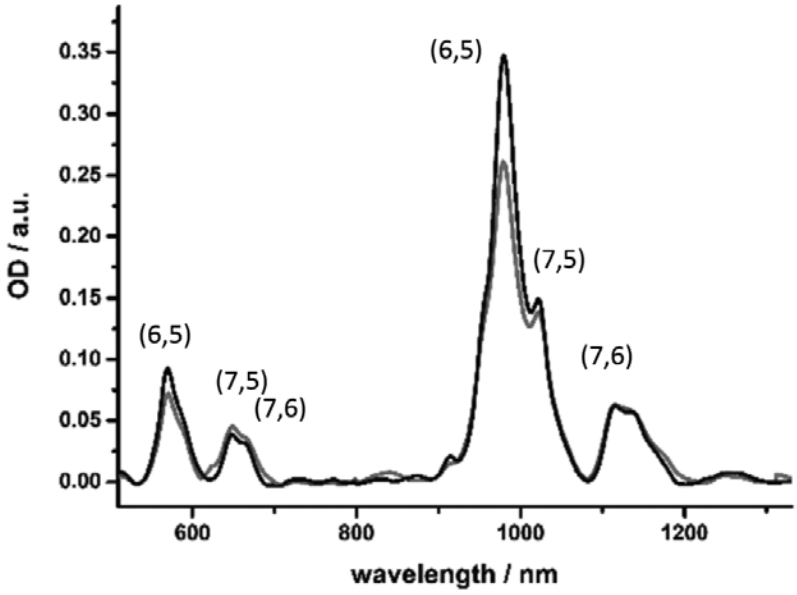


Fig S 11 UV-vis-NIR spectrum for (6,5)-enriched SWNTs.[1]

Reference

1. E. Martinez-Perinan, A. de Juan, Y. Pouillon, C. Schierl, V. Strauss, N. Martin, A. Rubio, D. M. Guldi, E. Lorenzo, E. M. Perez, *Nanoscale* **2016**, *8*, 9254-9264.