Responsive cross-linked supramolecular polymer network: hierarchical supramolecular polymerization driven by cryptand-based molecular recognition and metal-coordination

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Electronic Supplementary Information (8 pages)

1. Materials and Methods

2[S1] was synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{1}H NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P{^{1}H} NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The two-dimensional diffusion-ordered (2D DOSY) NMR spectra were recorded on a Bruker DRX500 spectrometer. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system or a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. The sample for SEM image was prepared by drawing out macroscopic fibers from highly concerntrated CH_3CN/CH_2Cl_2 (1:1, *v*/*v*) solution of CSPN ($c \approx 1.00$ M) and then placing them on silicon wafer.

2. *^{1}H NMR and ^{31}P NMR spectra of* ***2***

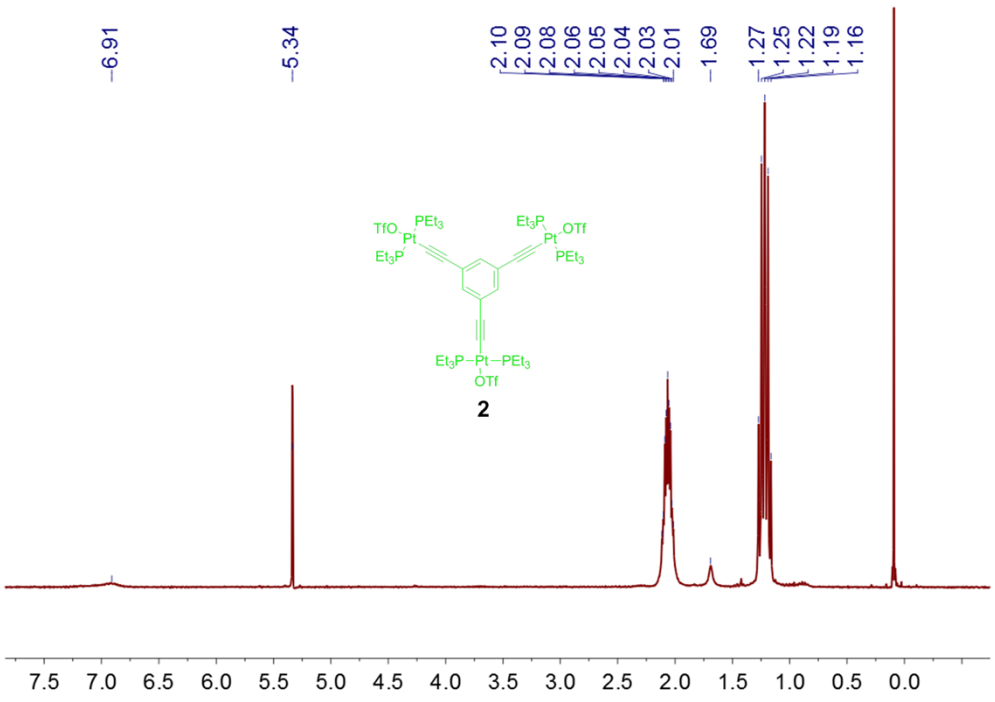


Figure S1. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 293 K) of **2**.

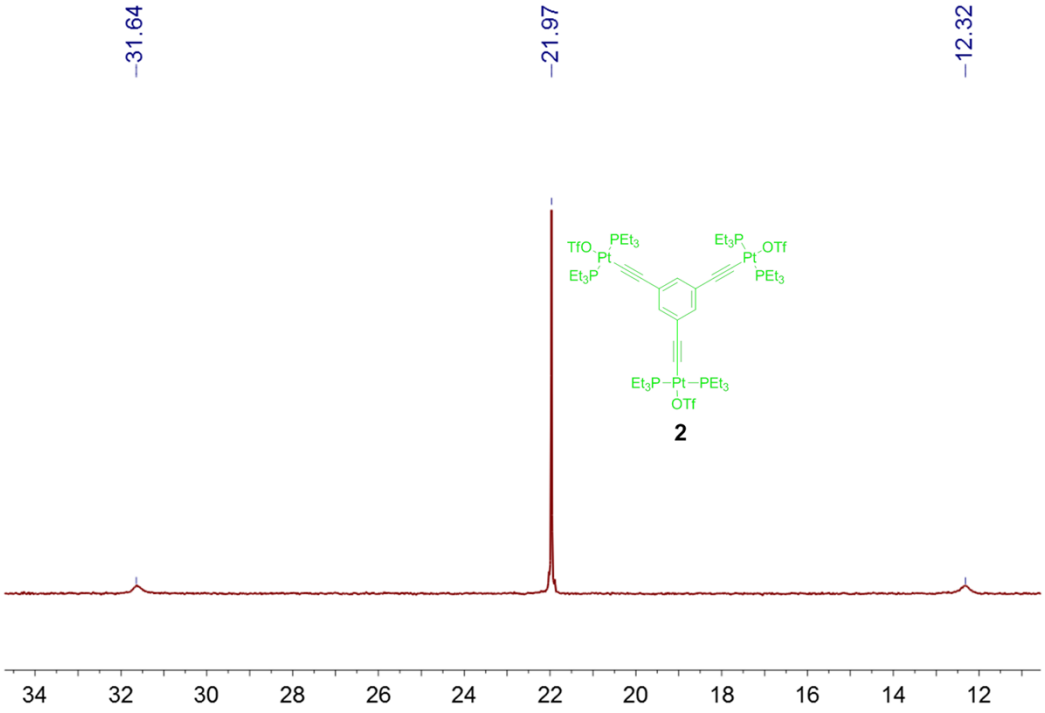
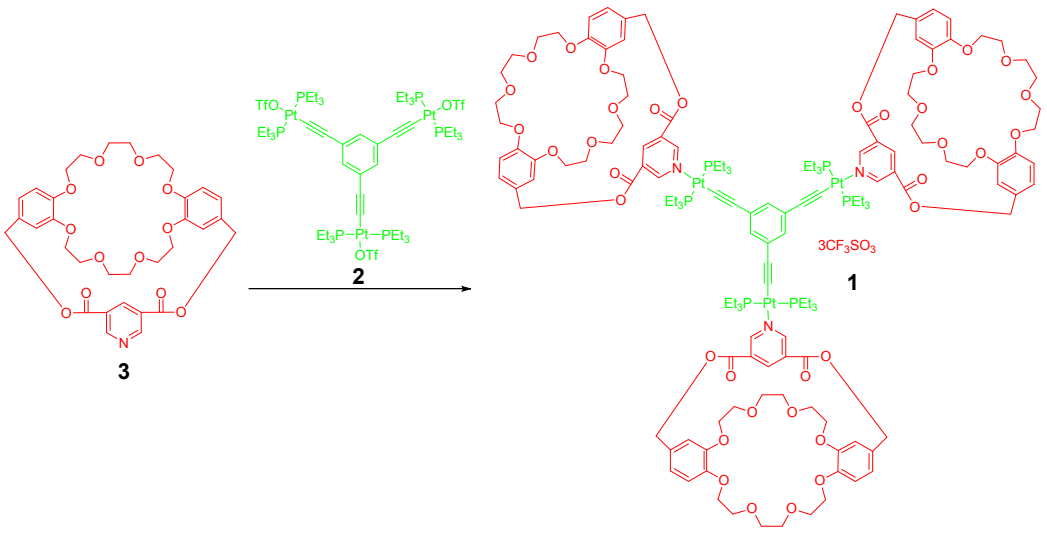


Figure S2. ^{31}P{^{1}H} NMR spectrum (161.8 MHz, CD_2Cl_2, 293 K) of **2**.

*3. Synthesis of tri-cryptand **1***

Scheme S1. Synthesis of tri-cryptand host **1**



Cryptand **3** (9.59 mg, 15.0 mM) and **2** (6.18 mg, 5.00 mM) were mixed together in CD_2Cl_2 at room temperature for 30 minutes to give host **1**. The ^{1}H NMR spectrum of **1** is shown in Figure S3. ^{1}H NMR (400 MHz, CD_2Cl_2, 293K) δ (ppm): 9.29–9.30 (m, 6H), 8.64 (s, 3H), 6.74–6.99 (m, 21H), 5.13–5.22 (m, 12H), 4.01–4.06 (m, 24H), 3.75–3.79 (m, 24H), 3.64–3.67 (m, 24H), 1.75–1.77 (m, 36H), 1.10–1.18 (m, 54H). The ^{31}P{^{1}H} NMR spectrum of **1** is shown in Figure S4. ^{31}P{^{1}H} NMR (s, 161.8 MHz, dichloromethane-d_2, 293K) δ (ppm): 15.57 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2284.6 Hz). ESI-MS for **1** is shown in Figure S5: *m*/*z* 1754.56 for [**1** – 2OTf]$^{2+}$, 1120.05 for [**1** – 3OTf]$^{3+}$

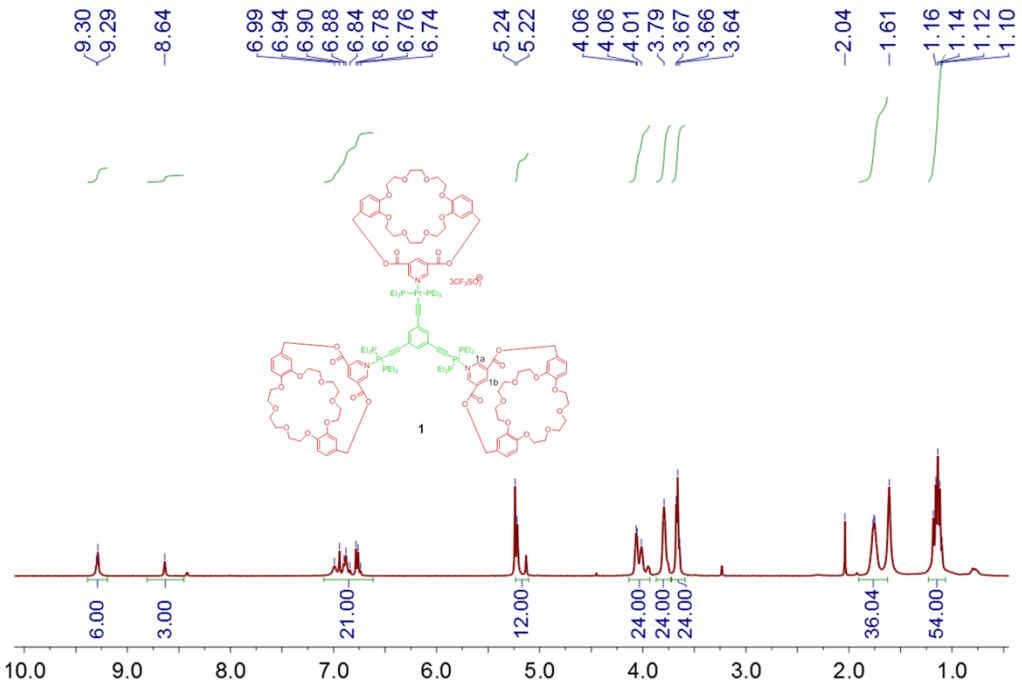


Figure S3. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 293 K) of **1**.

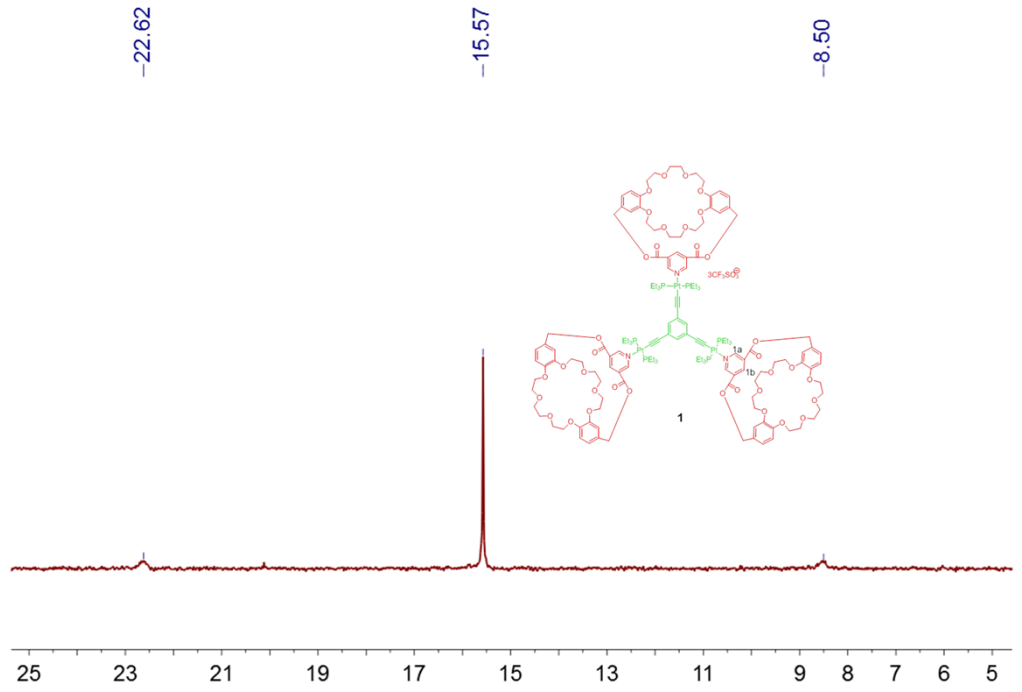
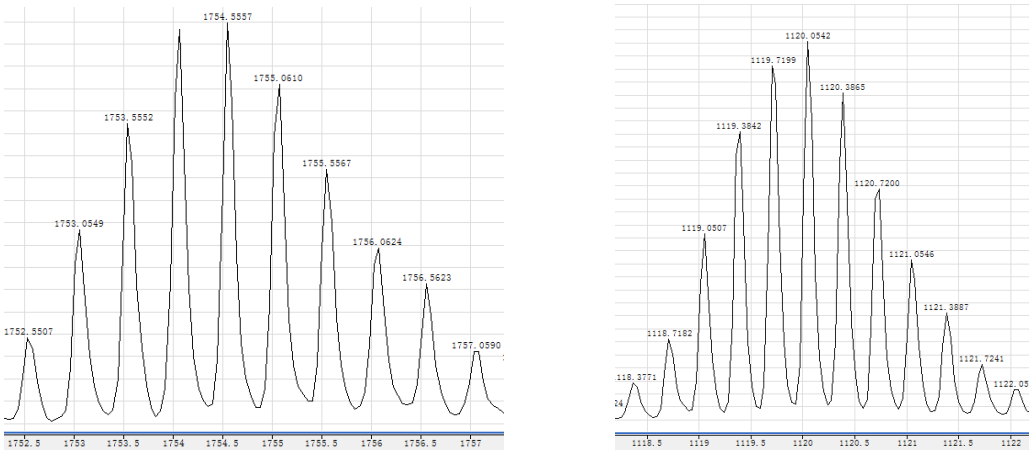


Figure S4. ^{31}P{^{1}H} NMR spectrum (161.8 MHz, CD_2Cl_2, 293 K) of **1**.



$[\mathbf{1} - 2\mathrm{OTf}]^{2+}$ $[\mathbf{1} - 3\mathrm{OTf}]^{3+}$

Figure S5. Electrospray ionization mass spectra of **1**.

*4. Comparison of ^{1}H NMR of **1** and **3** and ^{31}P NMR spectra of **1** and **2***

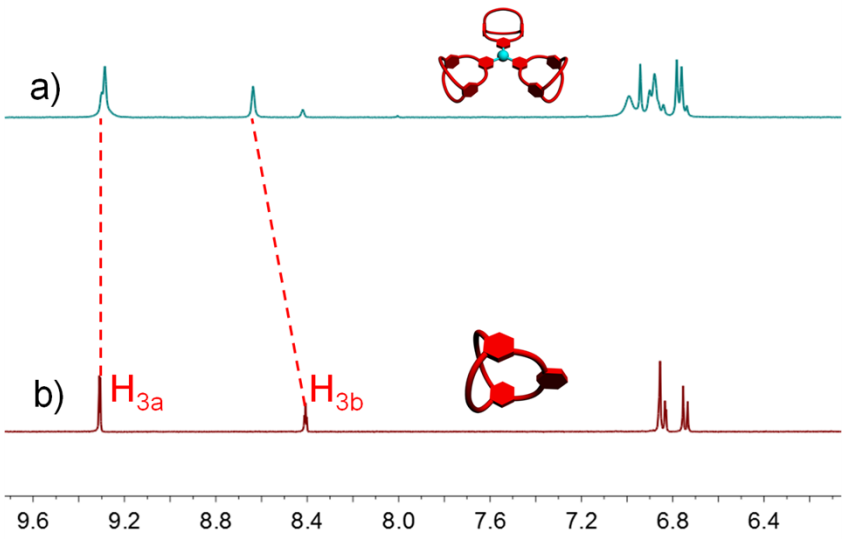


Figure S6. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 293 K) of (a) tri-cryptand host **1** and (b) cryptand **3**.

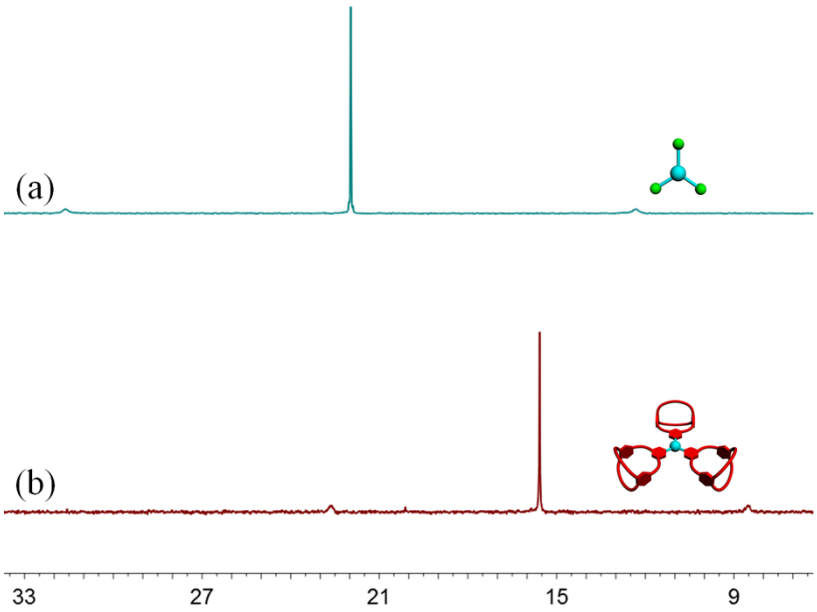


Figure S7. $^{31}P\{^{1}H\}$ NMR spectra (161.8 MHz, CD_2Cl_2, 293 K) of (a) tri-arm acceptor **2** and (b) tri-cryptand host **1**

5. Partial ^{1}H NMR spectra of $\mathbf{3}_2\supset\mathbf{4}$

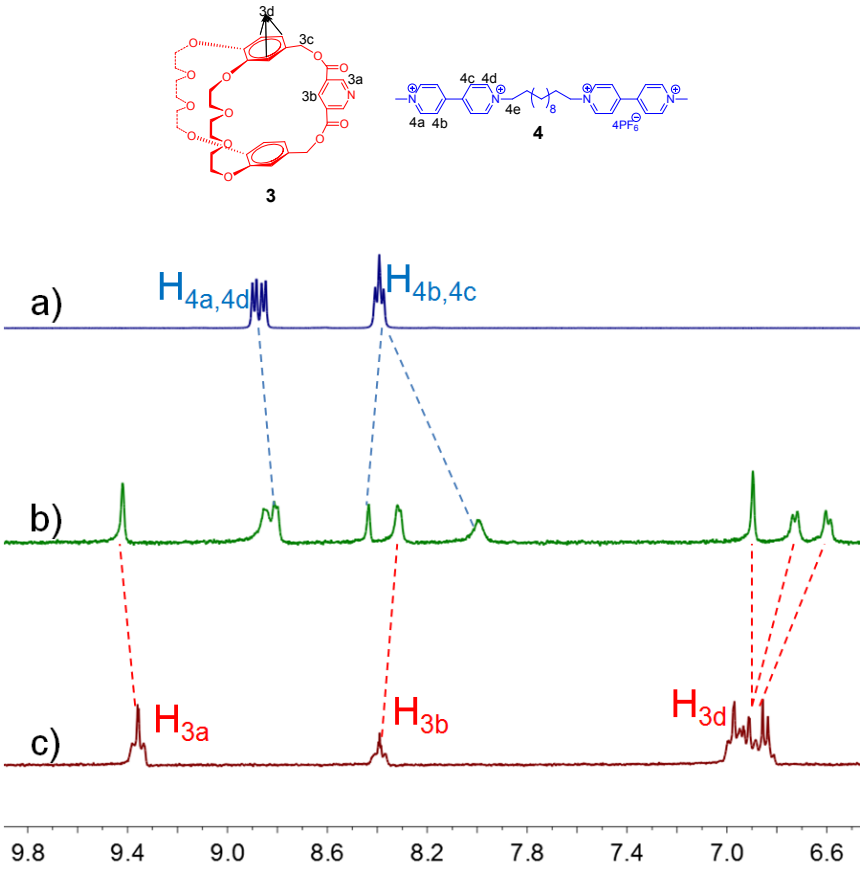


Figure S8. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2/CD_3CN (1:1, *v*/*v*), 293 K): (a) 4.00 mM **4**; (b) 8.00 mM **3** + 4.00 mM **4**; (c) 8.00 mM **3**.

6. LRESI mass spectrum of $\mathbf{3}_2\supset\mathbf{4}$

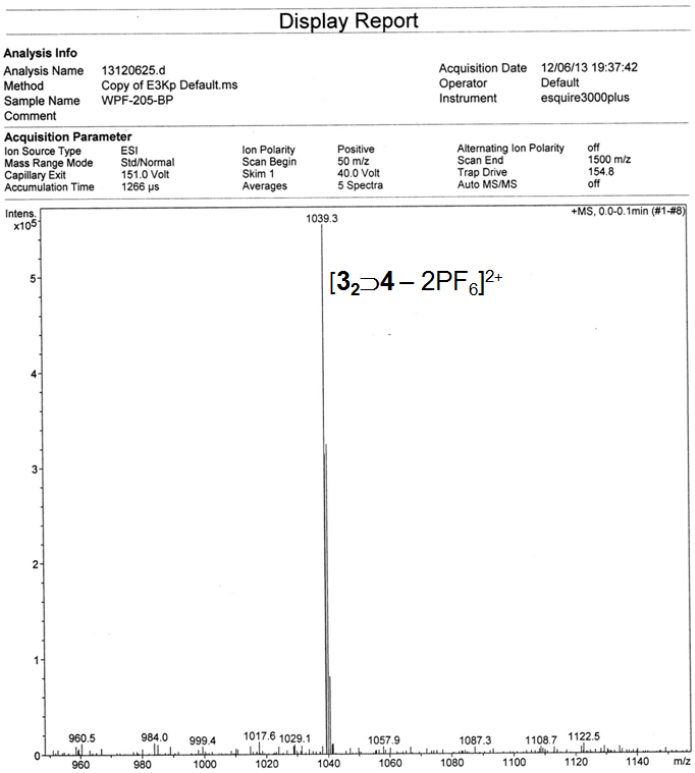


Figure S9. LRESI mass spectrum of $\mathbf{3}_2\supset\mathbf{4}$.

7. Diffusion coefficient D of ***1*** + ***4***, ***1*** + ***4*** + KPF_6, *and* ***1*** + ***4*** + KPF_6 + *DB18C6*

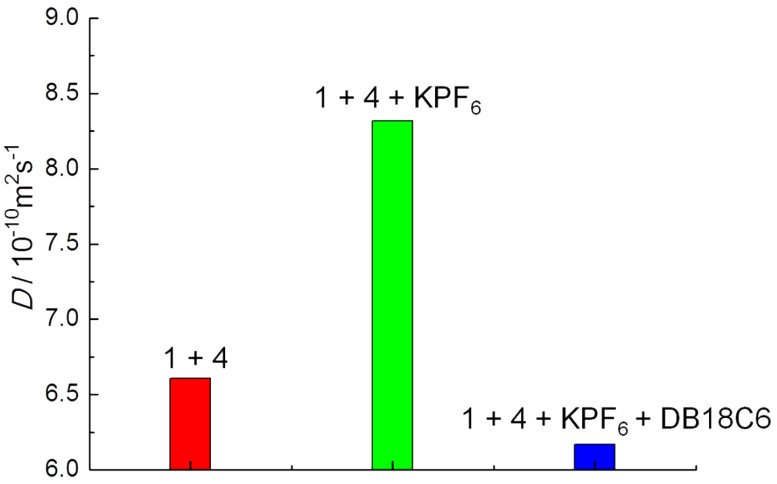


Figure S10. Diffusion coefficient *D* (400 MHz, CD_2Cl_2/CD_3CN (1:1, *v*/*v*), 293 K) of **1** + **4**, **1** + **4** + KPF_6, and **1** + **4** + KPF_6 + DB18C6 at 5.00 mM.

Reference:

S1. P. J. Stang, B. Olenyuk, J. Fan and A. M. Arif, *Organometallics*, 1996, **15**, 904–908.