Supramolecular Cruciforms

Supporting Information

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Materials and Methods

All chemicals were purchased from Aldrich Chemical, Acros, or Fisher Scientific and used as received unless otherwise specified. THF was dried via passage through Cu_2O and alumina columns. All glassware was flame dried or placed in an oven overnight at 130 °C. Column chromatography was performed with Premium Rf grade silica gel 60 Å, 40 – 75 μm (200 x 400 mesh) from Sorbent Technologies and the indicated eluant. Compounds were analyzed by use of UV light (254 nm). Melting points were determined with a Mel-Temp II apparatus fitted with a Fluke $51^{K/J}$ digital thermometer and are uncorrected. NMR spectra were recorded at 298 K on a Varian Mercury spectrometer (^{1}H = 300 MHz, ^{13}C NMR = 75 MHz). Chemical shifts are reported in parts per million (ppm), using residual solvent as an internal standard. Data reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), coupling constants, and integration. All fluorescence spectra were acquired on a Shimadzu RF-5301PC spectrofluorophotometer and acquired in a triangular quartz cuvette to minimize spectral artifacts (specifically self-absorption). Viscosimetry measurements were done in HPLC grade DMF, in a Cannon-Ubbelohde semi-micro type viscometer No. 100 L182, timed with a stopwatch at 25 °C. Mass spectral analyses were provided by the Georgia Institute of Technology Mass Spectrometry Facility. Elemental analyses were conducted at Atlantic Microlab, Inc. in Norcross, GA. Compound **6** was prepared according to a previous literature procedure.[1]

Experimental Procedures

Procedure for the preparation of cruciform 1: complex 2 solutions for fluorescence spectroscopy:

A stock solution of Cruciform **1** (0.0017 M) was prepared by dissolving **1** (24.9 mg, 0.042 mmol) in $CHCl_3$ (25.0 mL). A stock solution of bis-Pd-pincer complex **2** (0.0055 M) was prepared by dissolving **2 (**56.4 mg, 0.055 mmol) in $CHCl_3$ (10.0 mL). Solutions for measurement were then prepared as outlined in Table 1:

Supplemental Table 1

Equivalents of **2**	Stock Solution of **1** (μL)	Concentration of **1** (mM)	Stock Solution of **2** (μL)	Concentration of **2** (mM)	$CHCl_3$ (μL)
0.0	100	0.081	0	0	2000
0.8	100	0.081	24	0.0648	1976
1.6	100	0.081	48	0.130	1952
2.7	100	0.081	81	0.219	1919
3.4	100	0.081	102	0.275	1898
3.7	100	0.081	111	0.300	1889
3.9	100	0.081	117	0.316	1883
4.2	100	0.081	126	0.340	1874
4.5	100	0.081	135	0.365	1865
8.0	100	0.081	240	0.648	1760
10.0	100	0.081	300	0.810	1700

Spectra were recorded and are presented as Fig. 2 in the text. Spectra were also normalized to highlight the observed bathochromic shift (Supplemental Fig. 1).

Procedure for the preparation of cruciform 1: complex 4 solutions for fluorescent spectroscopy:

As a model system, cruciform **1** was titrated with mono-Pd-pincer complex **4**. A stock solution of **1** (0.0017 M) was prepared by dissolving **1** (49.9 mg, 0.083 mmol) in $CHCl_3$ (50 mL). A stock solution of mono-Pd-pincer complex **4** (0.0104 M) was prepared by dissolving **4** (60.9 mg,

0.104 mmol) in a mixture of $CHCl_3$ (9 mL) and DMF (1 mL). Solutions for measurement were then prepared as outlined in Table 2:

Supplemental Table 2

Equivalents of **4**	Stock Solution of **1** (mL)	Concentration of **1** (mM)	Stock Solution of **4** (μL)	Concentration of **4** (mM)	$CHCl_3$ (mL)
0.0	2.0	0.154	0	0	20.0
0.8	2.0	0.153	256	0.122	20.0
1.0	2.0	0.152	320	0.152	20.0
1.1	2.0	0.152	352	0.167	20.0
1.2	2.0	0.152	384	0.182	20.0
1.3	2.0	0.152	416	0.198	20.0
1.4	2.0	0.152	448	0.213	20.0
1.5	2.0	0.151	480	0.227	20.0
1.6	2.0	0.151	512	0.242	20.0
2.0	2.0	0.150	640	0.300	20.0
2.2	2.0	0.150	704	0.330	20.0
3.0	2.0	0.148	960	0.444	20.0
4.0	2.0	0.146	1280	0.584	20.0

Emission spectra were then collected (see Supplemental Fig. 2) and normalized to an intensity of 1000 to highlight the observed bathochromic shift and eliminate concentration effects (see Supplemental Fig. 3).

Procedure for the baseline subtraction of normalized fluorescence spectra of cruciform 1 self-assembled to mono-Pd-pincer 4:

The normalized emissions of Supplemental Figure 3 were excessively noisy. A spectrum of a triangular cuvette filled with a control solution of mono-Pd-pincer complex **4** was collected (Supplemental Fig. 4, green trace). When plotted against the raw emission data gathered (Supplemental Fig. 4, brown trace), it becomes obvious that this is the origin of the noise present in these raw emission spectra. A baseline subtraction was performed to remove these artifacts in the emission spectra (Supplemental Fig. 4, blue trace). The data was then normalized to

eliminate concentration effects (Supplemental Fig. 4, red trace). These corrected spectra are presented in the main text as Fig 3.

Procedure for the preparation of cruciform 1: complex 2 solutions with PPh_3 for fluorescence spectroscopy:

To qualitatively examine the binding of **1** to **2** and to assess any solvatochromic shift resulting from the addition of the polar metal complex **2**, we exposed solutions of **3** (supramolecular complex of **1** and **2)** to triphenylphosphine (PPh_3) and measured the resulting emission spectra. A stock solution of **1** (0.0017 M) was prepared by dissolving **1** (49.9 mg, 0.083 mmol) in $CHCl_3$ (50 mL). A stock solution of bis-Pd-pincer complex **2** (0.0083 M) was prepared by dissolving **2** (68.6 mg, 0.066 mmol) in a mixture of $CHCl_3$ (6 mL) and DMF (2 mL). A stock solution of PPh_3 (0.0089 M) was prepared by dissolving PPh_3 (20.9 mg, 0.080mmol) in $CHCl_3$ (9 mL). Solutions for measurement were then prepared as outlined in Supplemental Table 3:

Supplemental Table 3:

Solution	Stock Solution of **1** (μL)	[**1**] (mM)	Stock Solution of **2** (μL)	[**2**] (M)	Stock Solution of PPh_3 (μL)	[PPh_3] (M)	$CHCl_3$ (μL)	DMF (μL)
1	1000	0.282	0	0	0	0	3839	1200
1 + PPh_3	1000	0.282	0	0	2829	0.00417	1010	1200
1 + **2**	1000	0.282	1010	0.00139	0	0	2829	1200
1 + **2** + PPh_3	1000	0.282	1010	0.00139	2829	0.00417	0	1200

Fluorescence spectra were recorded and presented as Supplemental Figure 5. To highlight the observed shifts, this date was also normalized (see Supplemental Fig. 6). These solutions were also photographed under illumination at 365 nm (see Supplemental Fig. 7). **1** in a solution of $CHCl_3$/DMF emits at 447 nm. The addition of PPh_3 to a solution of **1** has no change on the emission. Upon addition of **2**, a bathochromic shift is observed (447-511 nm) as supramolecular

complex **3** forms. Upon the addition of PPh_3 to a solution of **3**, the emission reverts to that of cruciform **1** (446 nm). In addition, this demonstrates that the observed red-shift upon the addition of the pincer to cruciform is not the result of a change in solvent polarity.

(5-Methoxy-1,3-phenylene)bis(methylene)bis(phenylsulfane) (7):

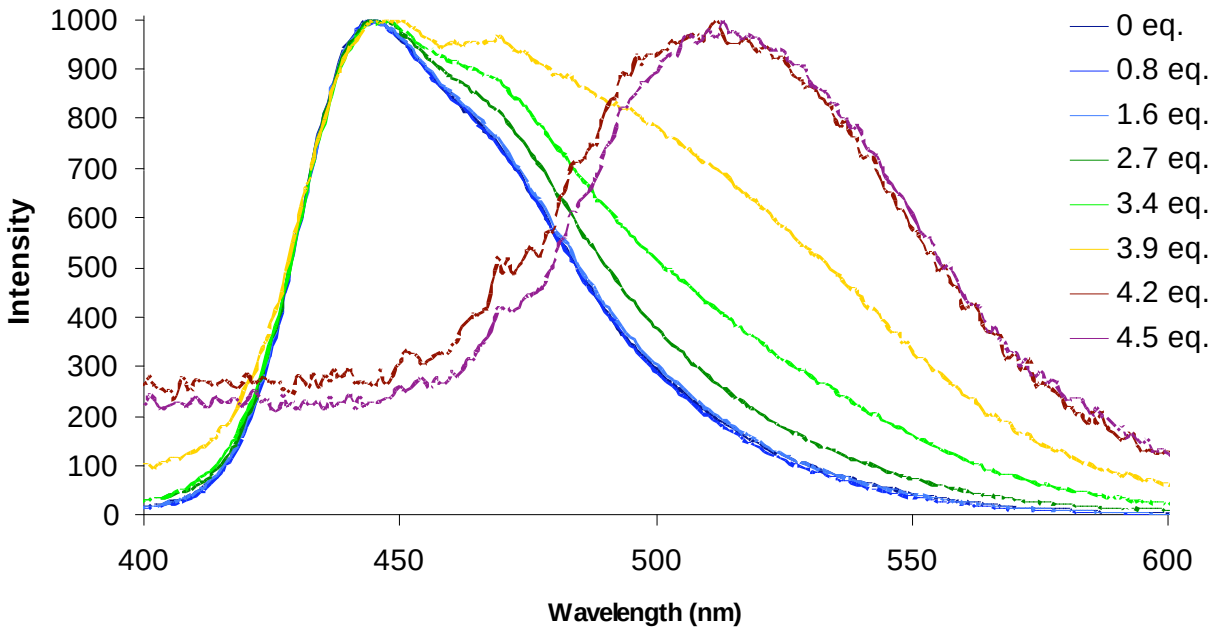
To a solution of **6** (1.12 g, 3.3 mmol) and CH_3I (0.70 g, 5.0 mmol) in anhydrous THF (50 mL) Cs_2CO_3 (1.29 g, 4.0 mmol) was added in one portion and let stir for twelve hours at 25 °C. Then, the solids were filtered off and the solvent was removed under reduced pressure. The crude oil was redissolved in EtOAc and purified by flash column chromatography (silica gel, eluant: 80:20 hexanes:EtOAc) and the product dried *in vacuo* to give a clear oil (1.10 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.34-7.13 (m, 10H, Ar H), 6.86 (s, 1H, Ar H), 6.70 (s, 2H, Ar H), 4.04 (s, 4H, Ar-CH_2-S), 3.71 (s, 3H, CH_3-O); ^{13}C NMR (75 MHz, $CDCl_3$,) δ: 159.7, 139.1, 136.4, 129.9, 128.9, 126.4, 121.7, 113.2, 55.2, 38.94; MS (EI, 70 eV) m/z: M^+ 352 (90), 243 (100), 210 (32), 134 (26), 91 (25); HRMS (EI, 70 eV) calcd for $C_{21}H_{20}OS_2$: 352.09459, found: 352.09556.

Pd-Cl (5-methoxy-1,3-phenylene)bis(methylene)bis(phenylsulfane) (8):

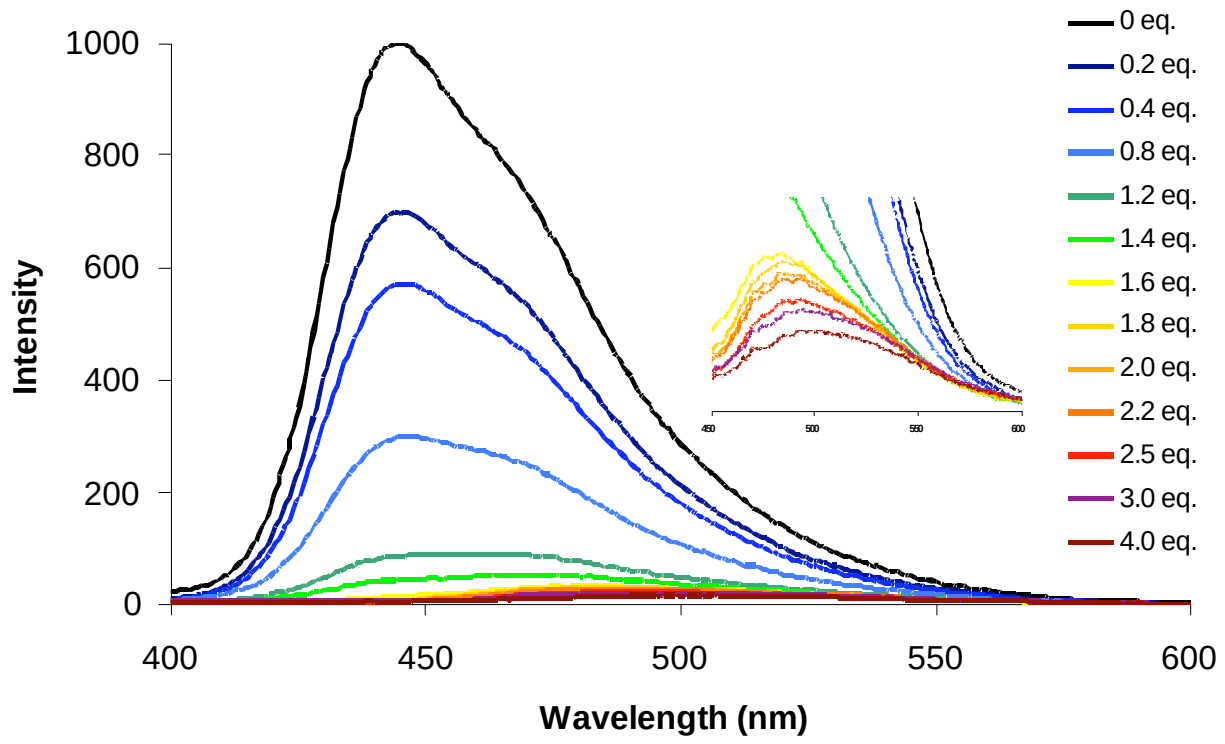
A solution of $PdCl_2(NCPh)_2$ (0.85 g, 2.2 mmol) and **7** (0.82 g, 2.2 mmol) in CH_2Cl_2:CH_3CN 1:1 (20 mL) was allowed to stir at 25 °C for 15 minutes becoming an opaque orange solution, at which time $AgBF_4$ (1.08 g, 5.55 mmol) was added. A precipitate formed immediately and the mixture was allowed to stir for an additional 30 minutes at 25 °C. During this time the reaction mixture changed from an orange to a yellow color. The reaction mixture was then diluted with CH_2Cl_2 (200 mL) and poured directly into a saturated aq. NaCl solution (200 mL) and stirred

overnight. The organic layer was separated, dried over $MgSO_4$, filtered through celite and the solvent removed under reduced pressure giving a crude yellow oil which was further purified by flash column chromatography (silica gel, (a) eluant: CH_2Cl_2 to flush out all non-palladated organics and then (b) eluant: 99:1 CH_2Cl_2:methanol to flush out the product) to yield the final product as a yellow foamy solid (1.07 g, 98%). The product was recrystallized from $CHCl_3$ forming large yellow crystals for X-ray structural analysis. ^{1}H NMR (300 MHz, d_6-DMSO) δ: 7.77-7.86 (m, 4H, Ar H), 7.40-7.49 (m, 6H, Ar H), 6.65 (s, 2H, Ar H), 4.73 (bs, 4H, Ar-CH_2-S), 3.65 (s, 3H, CH_3-O); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.3, 151.4, 150.0, 132.3, 131.3, 129.6, 129.5, 108.2, 55.2, 51.6; MS (ESI^+) 457.0; HRMS (ESI^+) calcd for $C_{21}H_{19}OPdS_2$: 457.9869, found: 457.9984 [the chlorine atom was labile under these ionization conditions]. Elemental analysis: calcd for $C_{21}H_{19}ClOPdS_2$: C, 51.12; H, 3.88; S, 13.

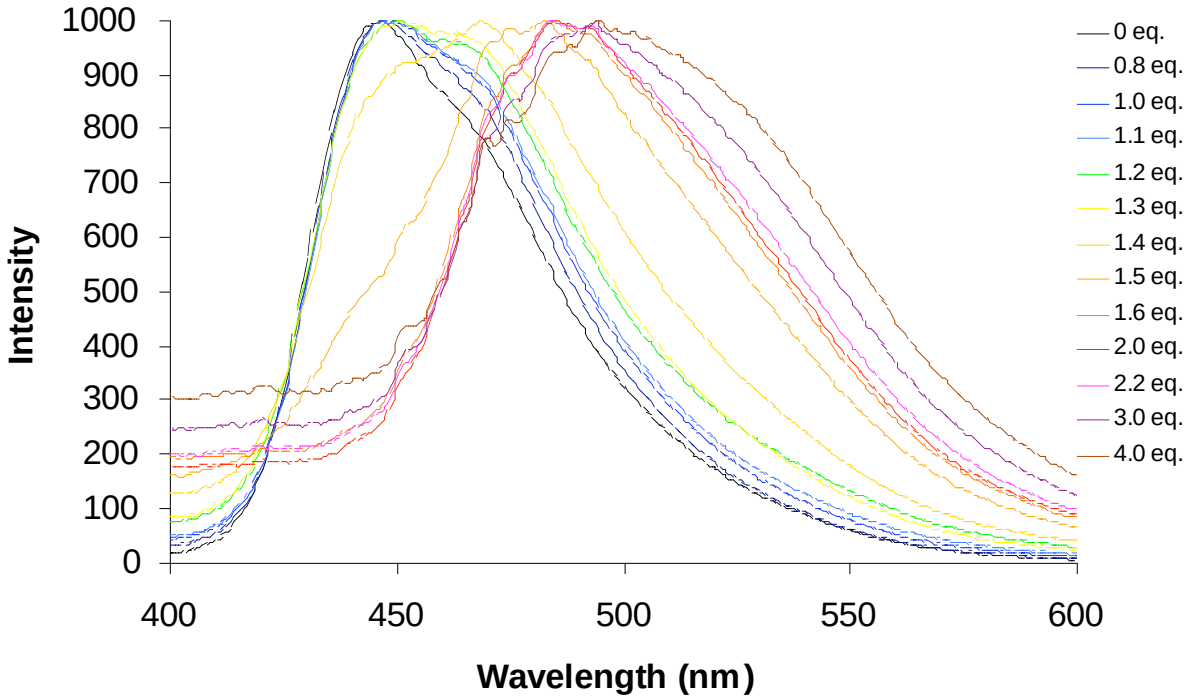
Figures and Schemes



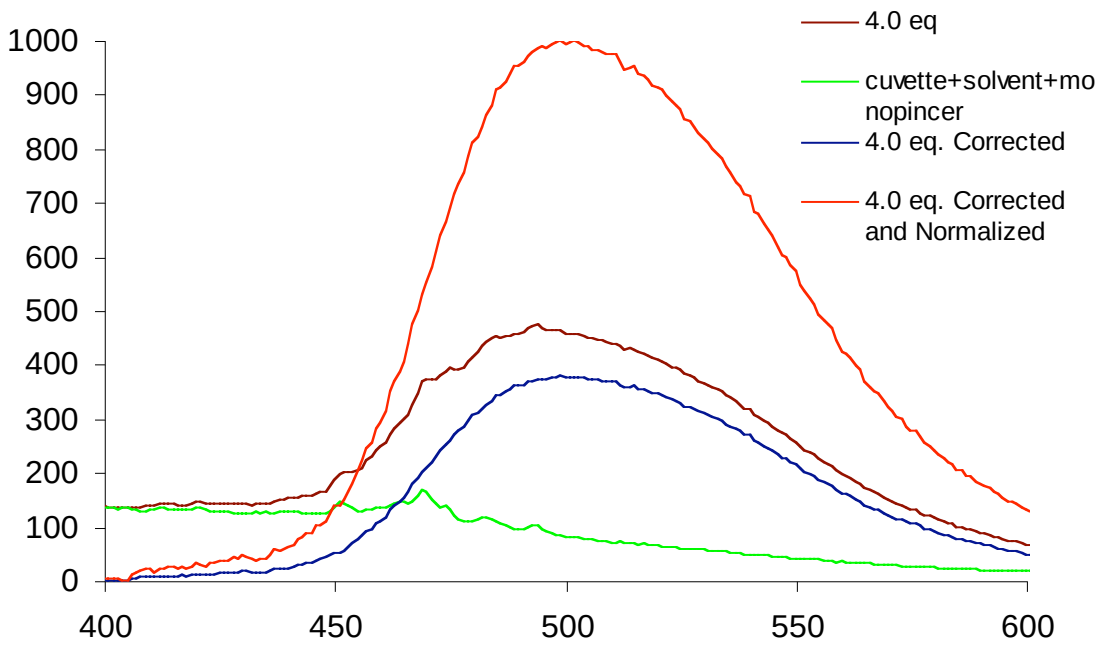
Supplemental Fig. 1. Normalized emission upon the addition of bis-Pd-pincer complex **2** to cruciform **1** in $CHCl_3$. Concentration of **1** in samples was 0.081 mM; equivalents (eq.) in the legend refer to the added amount of bis-Pd-pincer **2**. Spectra appear noisy at higher equivalents due to near baseline fluorescence intensity prior to normalization. Corresponds to Fig. 2 in the text.



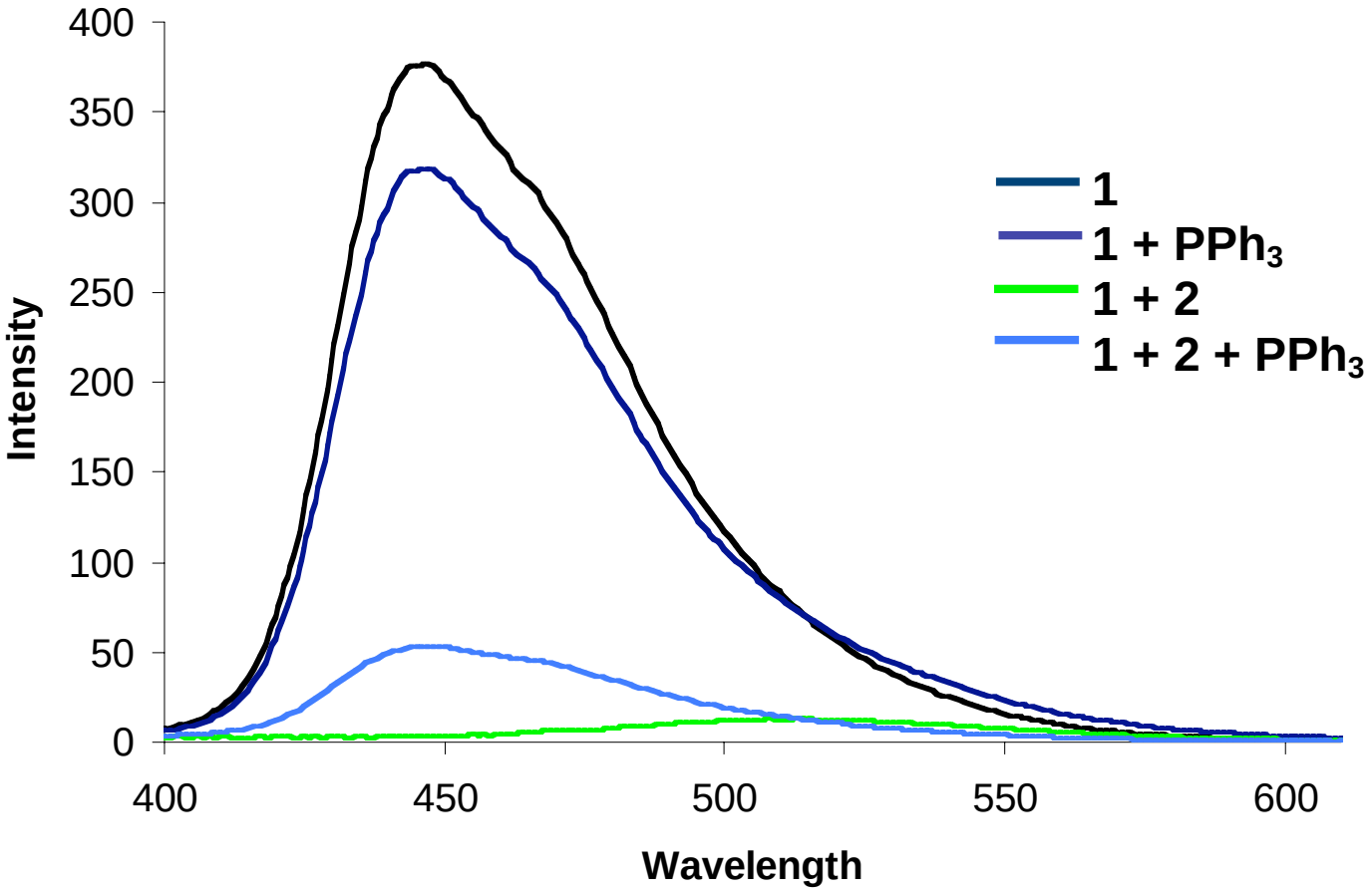
Supplemental Fig. 2. Shift in emission upon the titration of mono-Pd-pincer complex **4** into cruciform **1** in $CHCl_3$; the emission is bathochromically shifted (445-491 nm). Due to solubility and signal/noise issues, the concentration of **1** ranges from 0.154 mM (0 eq.) to 0.146 mM (4.0 eq.). Equivalents (eq.) in the legend refer to the added amount of mono-Pd-pincer **4**. Corresponds to Fig. 3 in the text; selected traces are shown here for clarity.



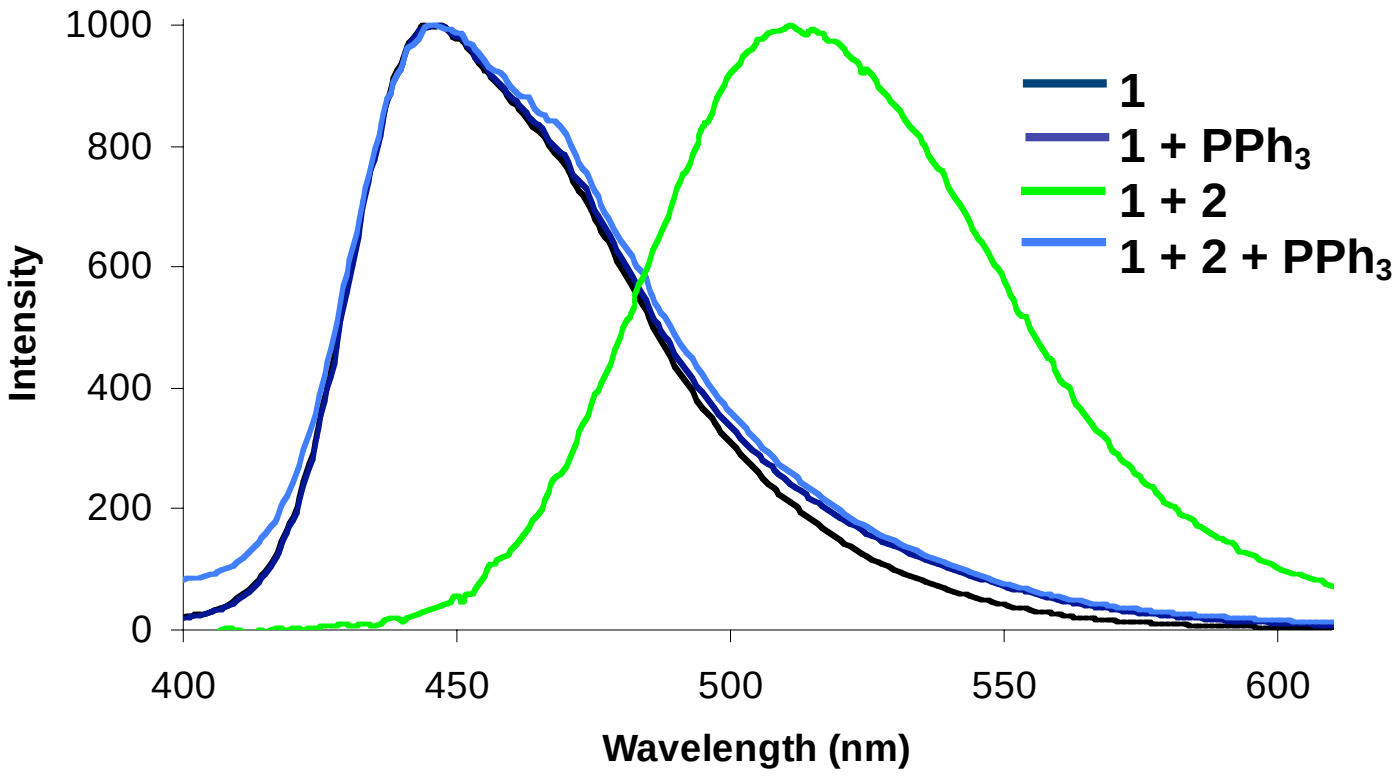
Supplemental Fig. 3. Normalized fluorescence spectra of raw experimental data for the addition of cruciform **1** self-assembled to mono-Pd-pincer complex **4** (note the noisy emission spectra). Due to solubility and signal/noise issues, the concentration of **1** ranges from 0.154 mM (0 eq.) to 0.146 mM (4.0 eq.). Equivalents (eq.) in the legend refer to the added amount of mono-Pd-pincer **4**. Corresponds to Fig. 3 in the text prior to baseline correction.



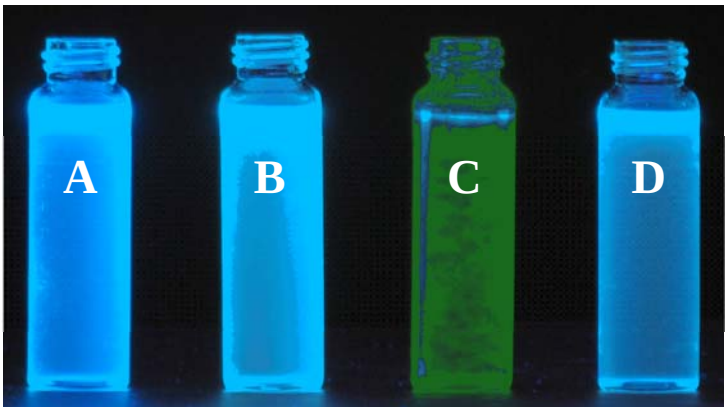
Supplemental Fig. 4. Baseline subtraction to remove spectral artifacts shown in Supplemental Fig. 3. Here, a representative example is presented graphically for the spectra of **1** with 4.0 equivalents of **4**. The spectra of a control solution of monopincer **4** (green trace) acquired in a triangular cuvette was subtracted from the raw emission data (brown trace). The resulting emission curve (blue trace) was then normalized (red trace).



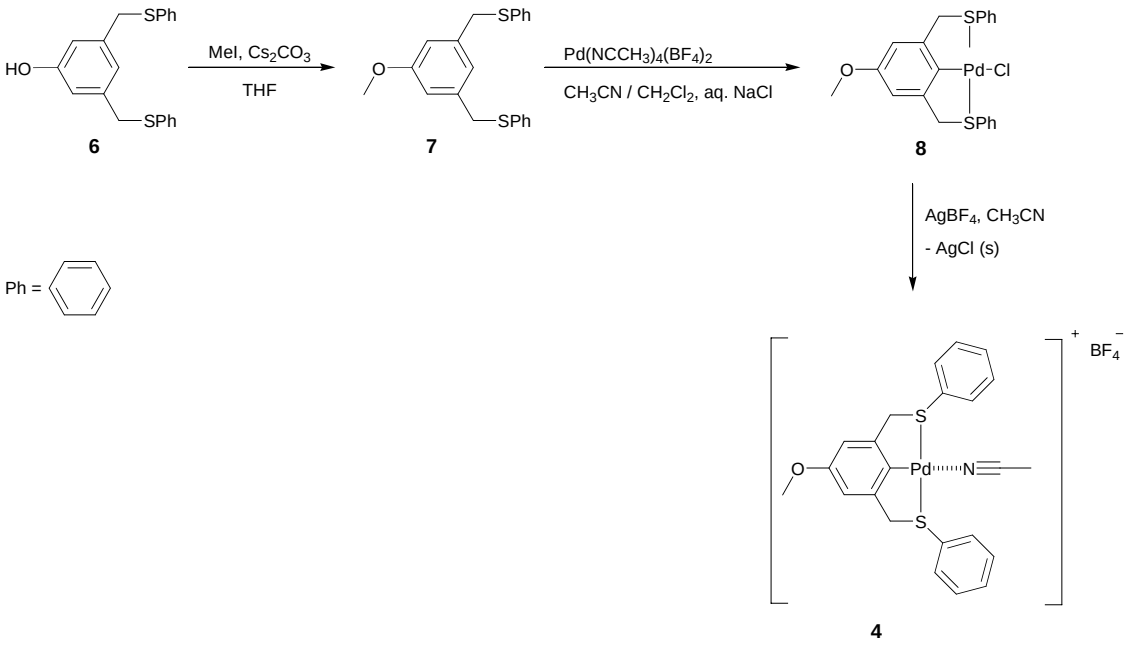
Supplemental Fig. 5. Effect of PPh_3 addition on the emission spectra of **1** and **1** + **2**. Upon addition of PPh_3 to a solution of **1** + **2** (λmax = 511 nm), the emission reverts to the blue emission of cruciform **1** (446 nm). The concentration of **1** in all samples was 0.282 mM.



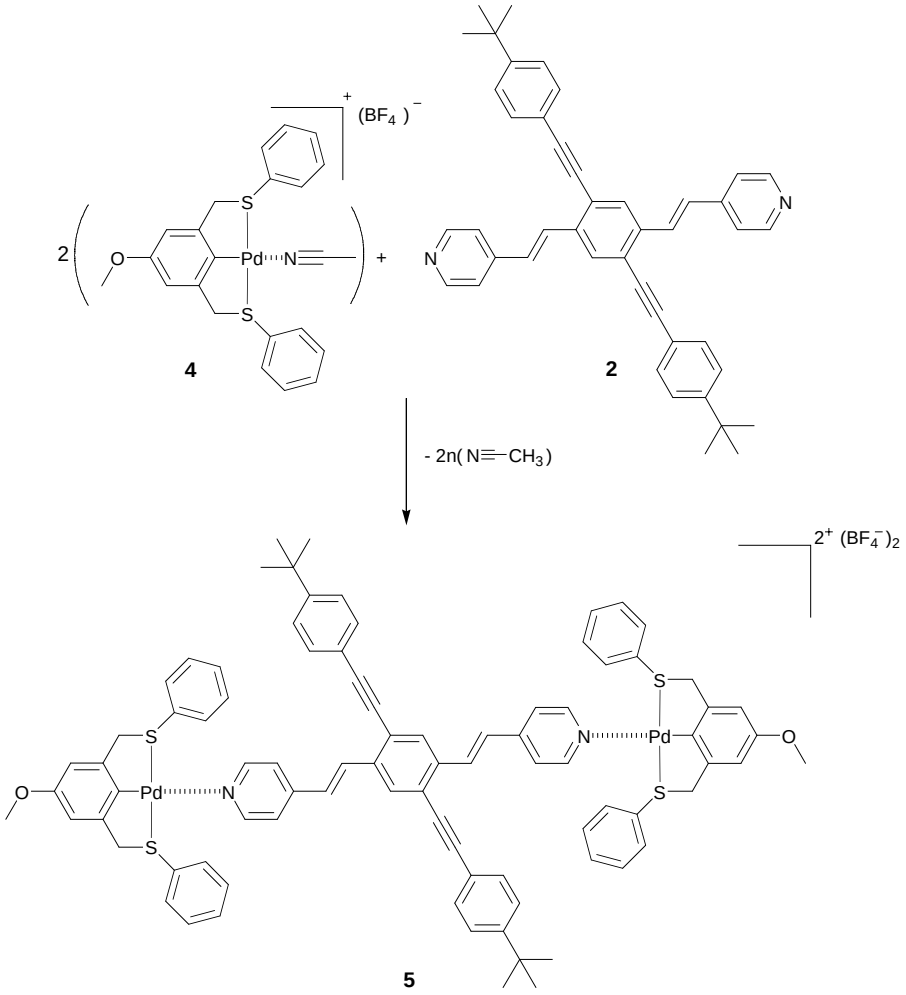
Supplemental Fig. 6. Normalized spectra demonstrating the effect of PPh_3 addition on the emission spectra of **1** and **1** + **2**. Upon addition of PPh_3 to a solution of **1** + **2** (λmax = 511 nm), the emission reverts to the blue emission of cruciform **1** (446 nm). The concentration of **1** in all samples was 0.282 mM.



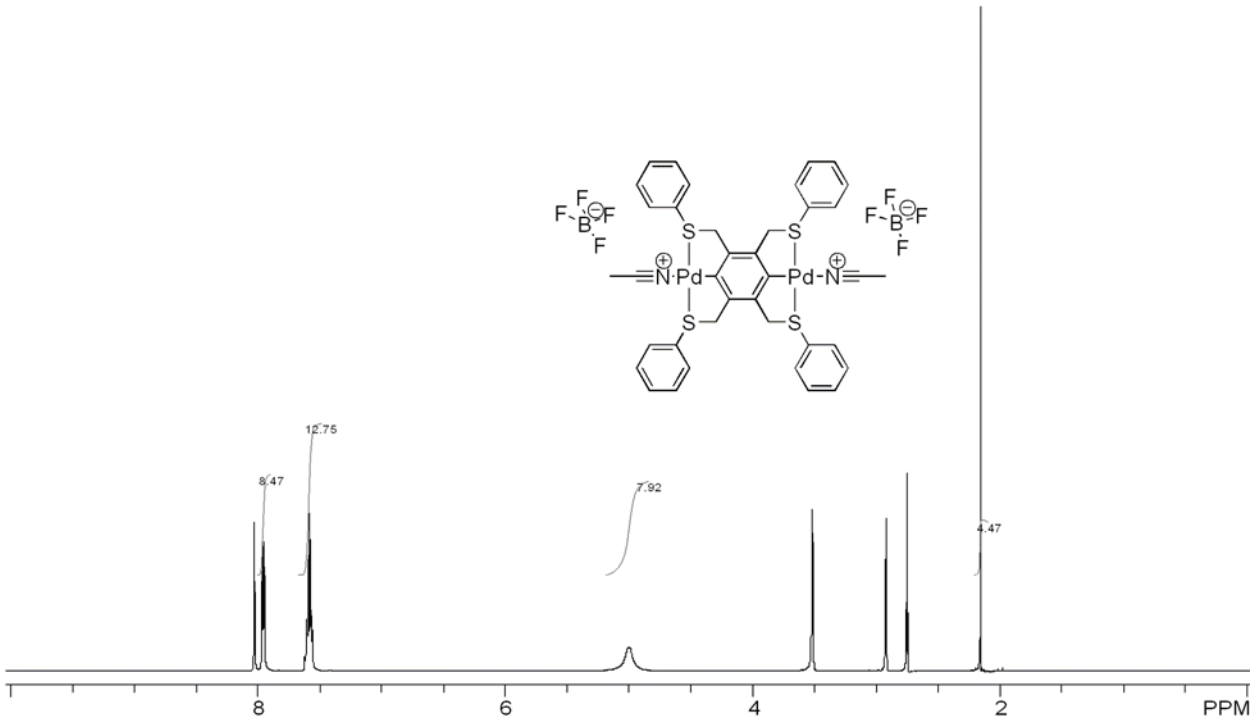
Supplemental Fig. 7. Effect of PPh_3 addition on the emission of **1** and **1** + **2**. Cruciform **1** in a solution of $CHCl_3$/DMF emits blue (vial A). No change is observed upon the addition of PPh_3 to **1** (vial B). When bis-Pd-pincer **2** is mixed with **1**, a bathochromic shift occurs and a green emission is observed (vial C). Addition of PPh_3 to a solution of **2** + **1** restores the blue emission of the cruciform (vial D). Photograph is taken under illumination at 365 nm.



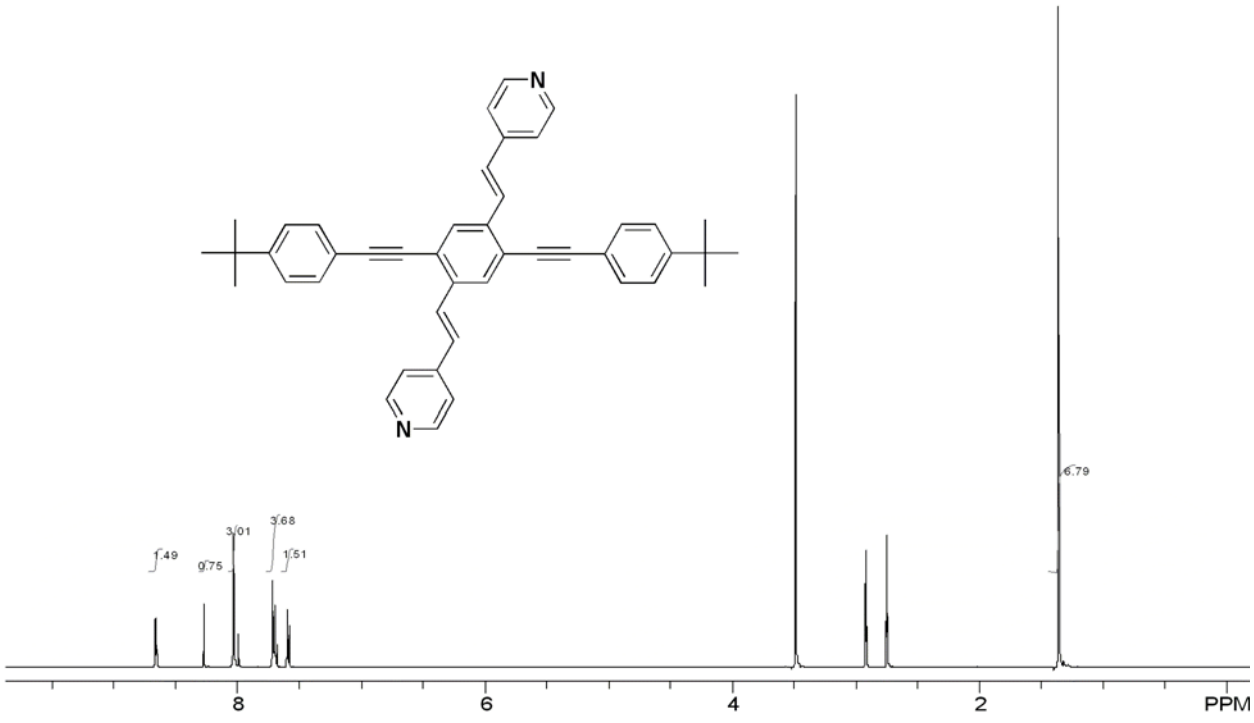
Supplemental Scheme 1. Synthesis of mono-Pd-pincer complex **4**.



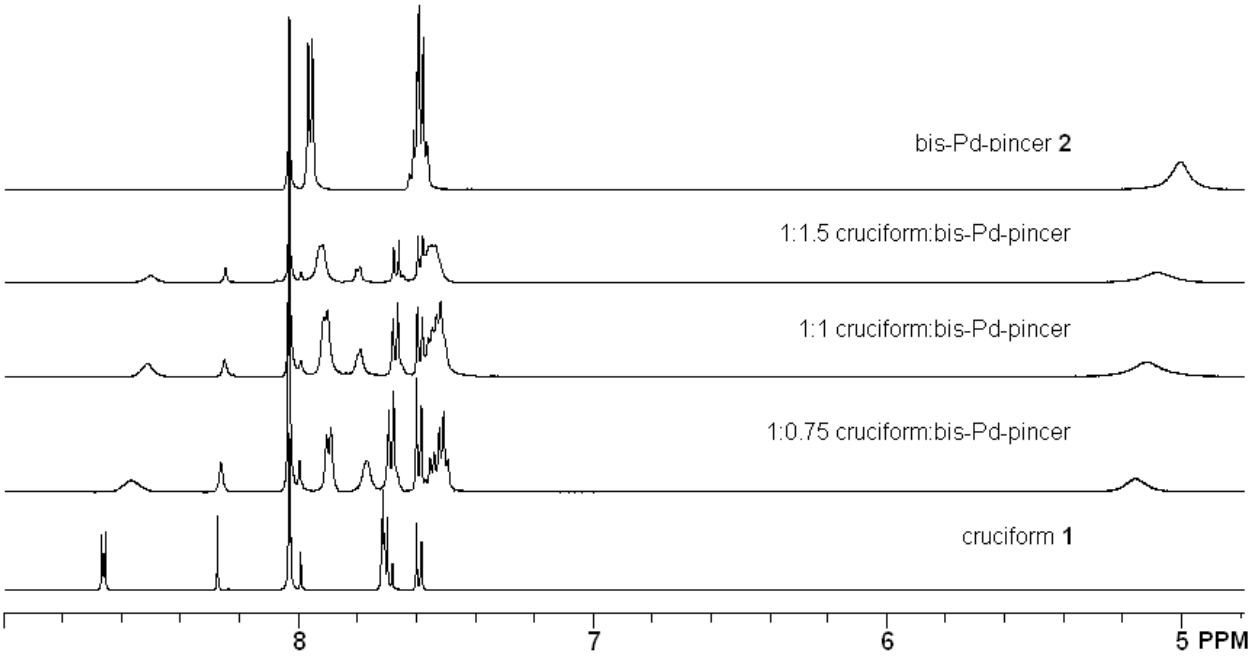
Supplemental Scheme 2. Small molecule self-assembly for the fluorescence model studies. Two equivalents of mono-Pd-pincer complex **4** coordinates to cruciform **2** forming model trimer complex **5**.



Supplemental Fig. 8. ^{1}H NMR bis-Pd-pincer **2** in d_7-DMF.



Supplemental Fig. 9. ^{1}H NMR cruciform **1** in d_7-DMF.



Supplemental Fig. 10. ^{1}H NMR overlay of bis-Pd-pincer **2** titrated into a d_7-DMF cruciform **1** solution.

References

1) W. T. S. Huck, F. C. J. M. Van Veggel, and D. N. Reinhoudt, *J. Mater. Chem.*, 1997, **7**, 1213.