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Supporting Information

p-Stacking Enhanced Dynamic and Redox-Switchable Self-Assembly of Donor-Acceptor Metallo-[2]Catenanes from Diimide Derivatives and Crown Ethers

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Supporting Information

Experimental Section

General Methods: Reagents were purchased from commercial sources or synthesized as described. Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV-light. Melting points were determined on an Electrothermal MEL-TEMP 3.0 apparatus and are uncorrected. UV/Visible spectra were obtained using a Varian Cary 100 Bio spectrophotometer. Proton and carbon nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) were recorded on a Bruker Avance500 II, using the deuterated solvent as lock and the residual solvent as internal standard. All chemical shifts are quoted using the *d* scale, and all coupling constants (*J*) are expressed in Hertz (Hz). The cold-spray ionization time-of-flight mass spectra (CSI-TOFMS) were acquired using an AccuTOF CS mass spectrometer (JMS-T100CS, JEOL, Tokyo, Japan) equipped with a CSI ion source. Electrospray mass spectra (ESI-MS) were measured on a Q-Tof Premier mass spectrometer from Micromass Technologies (now Waters Corporation). The microwave reaction was performed inside a Biotage Initiator 2.0 reactor. The naphthalene diimide derivative **1a**[s1] and the pyromelletic diimide **1b**[s2] were synthesized using a modified literature procedures where microwave radiation was used instead of conventional heating conditions. Crown ethers **4**,[s3] **5**,[s4] **6**[s5] and 2,7-diazapyrene (**3b**)[s6] were synthesized according to literature procedures.

Electrochemistry Methods: Electrochemistry experiments were executed using a Princeton Applied Research Potentiostat/Galvanostat model 263A, a glassy-carbon solid electrode as the working electrode, Ag/AgCl as the reference electrode and a platinum wire as the counter electrode. Electrochemical grade TBAPF$_6$ from Fluka was recrystallized twice from hot ethanol and dried under vacuum. The optically-transparent thin-layer electrochemical (OTTLE) cell was built in-house from a 1 mm quartz cuvette. The working electrode was a platinum mesh located at the sample beam with a platinum counter electrode and a Ag/AgCl wire pseudo-reference electrode.

General Procedure for the Assembly of Donor-Acceptor [2]Catenanes. To the mixture of diimide **1a** or **1b**, Pd(en)$(NO_3)_2$ (**2**), 2,7-diazapyrene (**3b**), and crown ether **4**, **5**, or **6** in the ratio of 1:2:1:1 (in the case of **5**, three equiv. was used) was added CD_3CN/D_2O (3:1). The mixture was stirred at 60 ^{o}C for 5 minutes to ensure the dissolution of all components, and filtered through a cotton plug to get the self assembled [2]catenanes. The filtrate was directly used for spectroscopic characterization. The solution of [2]catenane $\mathbf{10}^{4+}$ was further concentrated to remove the volatile solvent, followed by the addition of a saturated aqueous solution of NH_4PF_6. The resulting suspension was filtered, and the solid was rinsed thoroughly with H_2O and CH_2Cl_2 to give the [2]catenane in its PF_6 salt form.

[2]catenane 7·$4NO_3$: was assembled from **4** (3.0 mg, 4.7 µmol), **1a** (2.1 mg, 4.7 µmol), Pd(en)$(NO_3)_2$ (**2**) (2.7 mg, 9.4 µmol) and 2,7-diazapyrene (**3b**) (1.0 mg, 4.7 µmol). ^{1}H NMR (CD_3CN:D_2O = 0.9:0.3 mL, 500 MHz, 298 K): *d* = 9.38 (s, 2 H), 9.18 (br s, 2 H), 9.11 (br s, 2 H), 8.99 (s, 2 H), 7.91 (br s, 2H), 7.88 (br s, 2 H), 7.87 (d, *J* = 7.5 Hz, 2 H), 7.58 (d, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 9.0 Hz, 2 H), 7.11 (d, *J* = 9.0 Hz, 2 H), 6.22 (t, *J* = 8.0 Hz, 2 H), 6.10 (d, *J* = 8.0 Hz, 2 H), 5.93 (d, *J* = 8.0 Hz, 2 H), 5.37 (d, *J* = 13.5 Hz, 2 H), 5.13 (d, *J* = 13.5 Hz, 2 H), 5.13 (d, *J* = 8.0 Hz, 2 H), 4.71 (t, *J* = 8.0 Hz, 2 H), 4.63 (m, 2 H), 4.26–3.43 (m, 30 H), 3.10 (d, *J* = 8.0 Hz, 2 H), 2.97 (m, 4 H), 2.88 (m, 4 H); CSI-MS for $C_{80}H_{76}D_8N_{14}O_{26}Pd_2$: 877.2 $[M{-}2NO_3]^{2+}$, 564.1

$[M-3NO_3]^{3+}$, 542.8 $[M-3NO_3-HNO_3]^{3+}$, 438.4 $[M-4NO_3+3MeCN]^{4+}$, 428.1 $[M-4NO_3+2MeCN]^{4+}$, 417.9 $[M-4NO_3+MeCN]^{4+}$.

[2]catenane 8·4NO$_3$: was assembled from **5** (12.0 mg, 22.2 μmol), **1a** (3.3 mg, 7.4 μmol), Pd(en)(NO$_3$)$_2$ (**2**) (4.3 mg, 14.7 μmol) and 2,7-diazapyrene (**3b**) (1.5 mg, 7.4 μmol). ^{1}H NMR (CD_3CN:D_2O = 0.9:0.3 mL, 500 MHz, 298 K): *d* = 9.53 (s, 4 H), 8.99 (d, *J* = 6.5 Hz, 4 H), 8.14 (s, 4 H), 7.93 (s, 4 H), 7.67 (d, *J* = 6.5 Hz, 4 H), 5.22 (s, 4 H), 5.20 (s, 4 H), 4.34 (m, 4 H), 4.16 (m, 4 H), 3.98 (m, 4 H), 3.95 (m, 4 H), 3.70 (m, 4 H), 3.60 (m, 4 H), 3.19 (m, 4 H), 2.88 (m, 8 H), 2.77 (m, 4 H), 2.74 (s, 4 H). CSI-MS for $C_{72}H_{72}D_8N_{14}O_{26}Pd_2$: 827.2 $[M-2NO_3]^{2+}$, 795.7 $[M-2NO_3-HNO_3]^{2+}$, 530.8 $[M-3NO_3]^{3+}$, 523.1 $[M-3NO_3-HNO_3+MeCN]^{3+}$, 509.5 $[M-3NO_3-HNO_3]^{3+}$, 413.4 $[M-4NO_3+3MeCN]^{4+}$, 403.6 $[M-4NO_3+2MeCN]^{4+}$.

[2]catenane 9·4NO$_3$: was assembled from **6** (4.4 mg, 5.9 μmol), **1a** (2.7 mg, 5.9 μmol), Pd(en)(NO$_3$)$_2$ (**2**) (3.4 mg, 11.8 μmol) and 2,7-diazapyrene (**3b**) (1.2 mg, 5.9 μmol). ^{1}H NMR (CD_3CN:D_2O = 0.9:0.3 mL, 500 MHz, 298 K): *d* = 9.62–9.58 (m, 2H), 8.85–8.7 (m, 2 H), 8.07–7.99 (m, 2 H), 7.91–7.82 (m, 2 H), 7.56–7.48 (m, 2 H), 7.05 and 6.92 (d, *J* = 8.0 Hz, 2 H),6.83 and 6.74 (t, *J* = 8.0 Hz, 2 H), 6.36 and 6.30 (d, *J* = 8.0 Hz, 2 H),5.49 and 5.48 (s, 2 H), 5.27–5.16 (m, 4 H), 3.97–3.73 (m, 36 H), 2.90–2.83 (m, 8 H). CSI-MS for $C_{78}H_{76}D_8N_{14}O_{26}Pd_2S_4$: 970.1 $[M-2NO_3+2MeCN]^{2+}$, 929.1 $[M-2NO_3]^{2+}$, 598.7 $[M-3NO_3]^{3+}$, 577.7 $[M-3NO_3-HNO_3]^{3+}$.

[2]catenane 10·4PF$_6$: was obtained from **4** (3.0 mg, 4.7 μmol), **1b** (1.9 mg, 4.7 μmol), Pd(en)(NO$_3$)$_2$ (**2**) (2.7 mg, 9.3 μmol) and 2,7-diazapyrene (**3b**) (1.0 mg, 4.7 μmol) after counterion exchange. ^{1}H NMR (CD_3CN, 500 MHz, 298 K): *d* = 9.60 (s, 2 H), 9.39 (d, *J* = 6.0 Hz, 2 H), 9.20 (d, *J* = 6.0 Hz, 2 H), 9.09 (s, 2 H), 7.91 (d, *J* = 6.0 Hz, 2 H), 7.81 (d, *J* = 6.0 Hz, 2 H), 7.60 (d, *J* = 9.0 Hz, 2 H), 7.21 (d, *J* = 9.0 Hz, 2 H), 6.68 (s, 2 H), 6.45 (t, *J* = 8.0 Hz, 2 H), 6.14 (d, *J* = 8.0 Hz, 2 H), 6.07 (d, *J* = 8.0 Hz, 2 H), 5.69 (d, *J* = 8.0 Hz, 2 H), 5.21 (t, *J* = 8.0 Hz, 2 H), 4.91 (m, 2 H), 4.84 (d, *J* = 14.0 Hz, 2 H), 4.68 (d, *J* = 14.0 Hz, 2 H), 4.45–3.73 (m, 30 H), 3.10 (m, 4 H), 2.95 (m, 4 H), 2.77 (d, *J* = 8.0 Hz, 2 H).

[**2]catenane 11**·4NO_3: was assembled from **5** (8.0 mg, 15 µmol), **1b** (2.0 mg, 5.0 µmol), Pd(en)$(NO_3)_2$ (**2**) (2.9 mg, 10 µmol) and 2,7-diazapyrene (**3b**) (1.0 mg, 5.0 µmol). ^{1}H NMR (CD_3CN:D_2O = 0.9:0.3 mL, 500 MHz, 298 K): *d* = 9.61 (s, 4 H), 9,06 (d, *J* = 6.5 Hz, 2 H), 8.04 (s, 4 H), 7.63 (d, *J* = 6.5 Hz, 2 H), 7.26 (s, 2 H), 5.29 (s, 4 H), 4.74 (s, 4 H), 4.32 (m, 4 H), 4.22 (m, 4 H), 3.20 (m, 4 H), 3.04 (m, 4 H), 2.88 (m, 8 H), 2.67 (s, 4 H).

CSI-MS characterization of the [2]catenanes

The sample solutions used for ^{1}H NMR spectroscopy were directly used for CSI-TOFMS characterization by 5-fold dilution with CH_3CN (HPLC grade). The solution was then delivered to the ion source by an infusion syringe pump at a flow rate of 5 µl/min. The CSI-TOFMS spectra were acquired using an AccuTOF CS mass spectrometer (JMS-T100CS, JEOL, Tokyo, Japan). The needle voltage was set at 2000V, orifice 1 voltage was set at 20V; orifice 2 voltage was 5V; Ring lenses voltage was 10V, the flow rate and temperature of nebulizing gas were 2.5L/min and -20 °C, respectively. The peaks voltage was set at 2500V, the other analyzer voltages were set to obtain sufficient resolution up to 6000 (50% peak). The detector voltage was set at 2500V. The mass range was from 100 to 3000, the spectrum-recording interval was 2 seconds and the data-sampling interval was 0.5 nanoseconds. The eight NH exchangeable protons were exchanged to ND. Consequently, an 8 Dalton difference from the expected molecular mass was observed for all tested samples. In all cases, there were extra fragments arising from the attachment of various CD_3CN molecules on the molecular ions under the cold-spray conditions. (See Figures S1-S3)

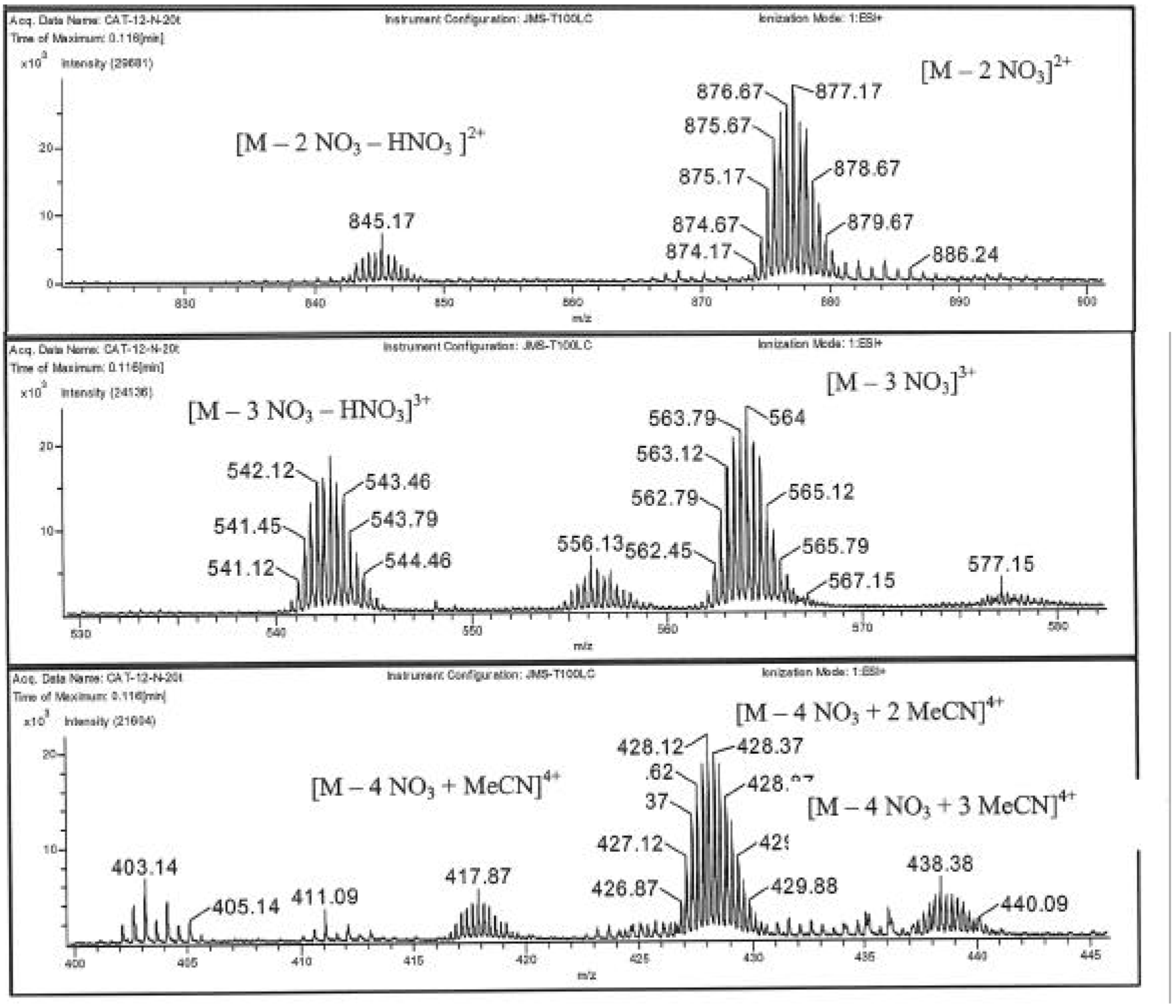

Figure S1: Assignment of molecular fragments in CSI-MS spectra of **7**•$4NO_3$.

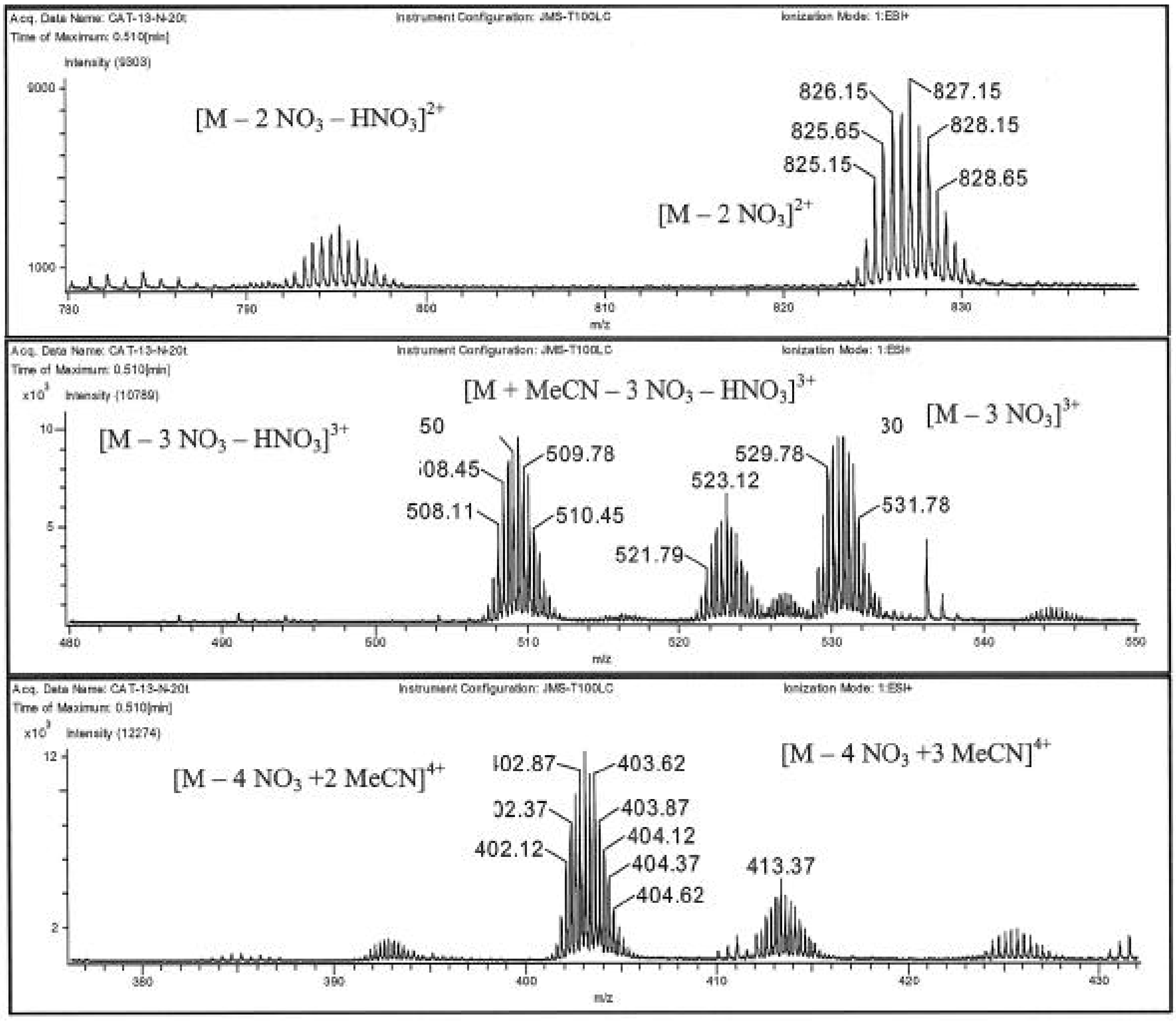

Figure S2: Assignment of molecular fragments in CSI-MS spectra of **8**•4NO_3.

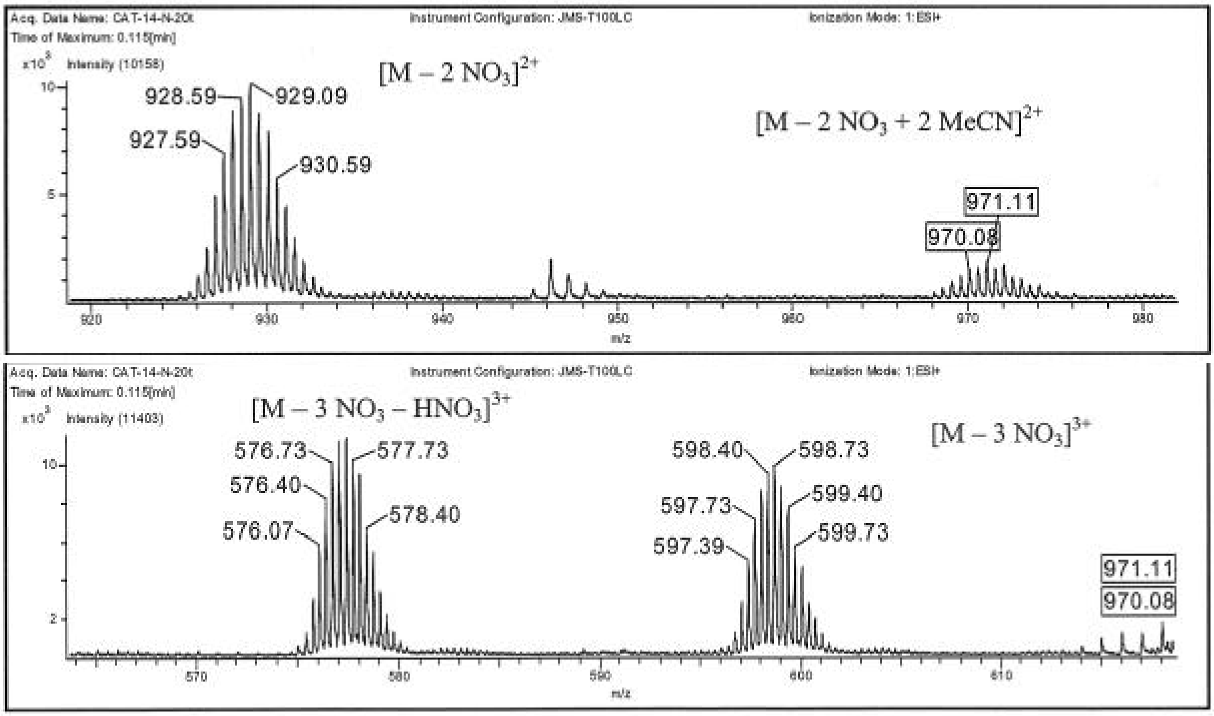

Figure S3: Assignment of molecular fragments in CSI-MS spectra of **9**•4NO_3.

Optimized Geometry of NDI-based metallocyclophane MC1 and PmI-based metallocyclophanes MC2

The geometry of the two metallocyclophanes were optimized using density functional theory calculations (B3LYP model).[s7]the ligand atoms were optimized using the 6-31G(d) basis set, while the Pd atoms were optimized using a LanL2DZ basis set where the effective core potential of Wadt and Hay (Los Alamos ECP) was included. [s8]

The optimized geometry of MC1 revealed (Figure S4a) a trapeziform cyclophane. The N-N distances for the NDI unit and the diazapyrene unit were 7.05 Å and 6.99 Å, respectively, indicating that the two p systems were similar in dimensions. The distance between the two centroids of the two p systems was 6.80 Å, ideal for the inclusion of an aromatic guest. As a result of the large radius of Pd atoms, the Pd-Pd distance (11.24 Å) was significantly longer than the C-C distance on the opposite edge (9.97 Å). Similar geometry was observed in the PmI-based MC2 (Figure S4b), except that the PmI unit was significantly shorter than diazapyrene in length (6.74 Å versus 6.99 Å).

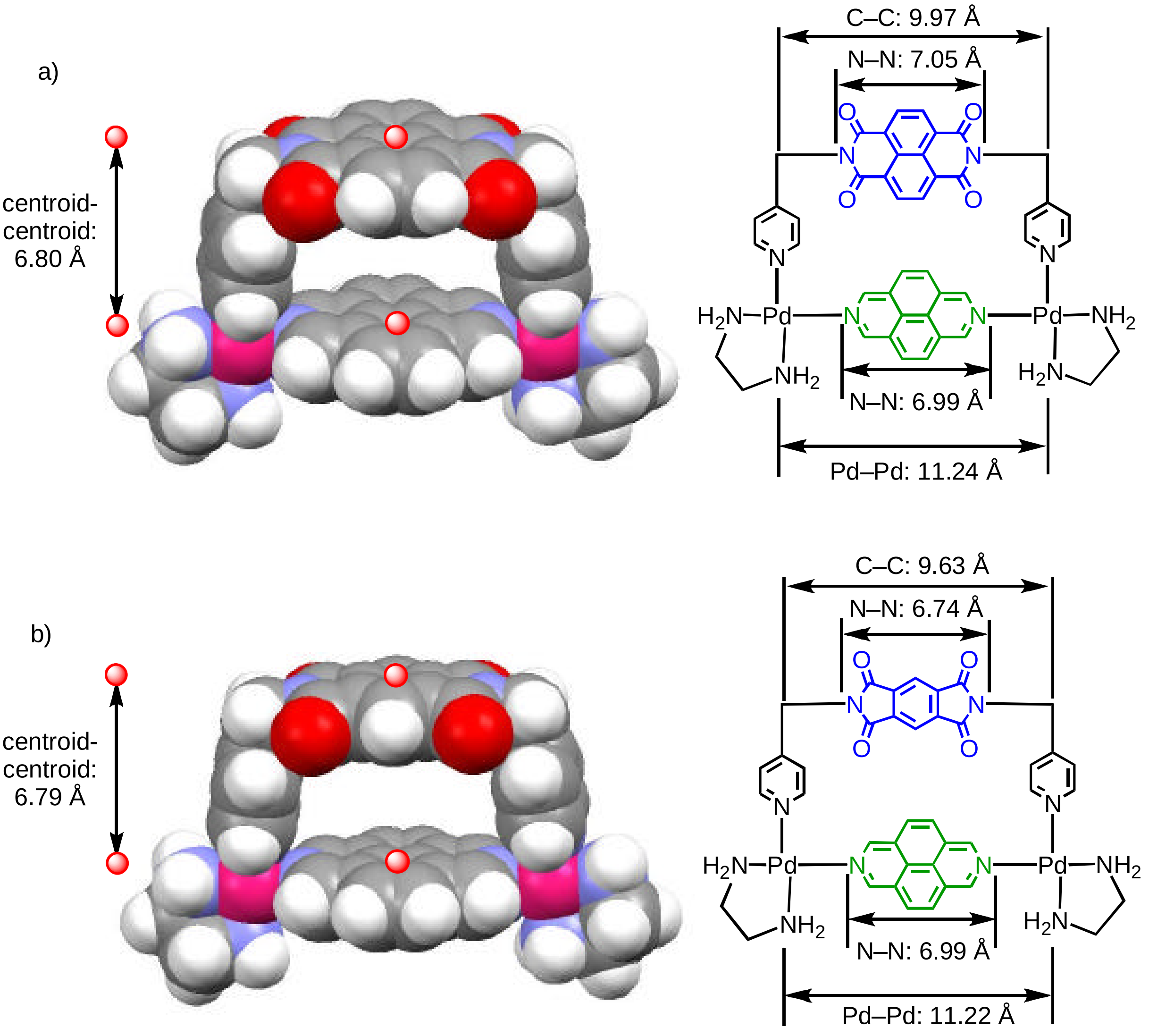

Figure S4: Optimized geometry and molecular formulae of a) MC1 and b) MC2.

UV-Vis-NIR spectroelectrochemistry of 9•4NO$_3$

The spectroelectrochemistry (SEC) experiment was carried out on a 1 mM solution of [2]catenane **9**•4NO$_3$ in an aqueous mixture of H_2O and CH_3CN (1:3). The slow scan rate CV (0.25 mV s^{-1}) show two oxidation peaks (inset to Figure S5) in the forward scan but on the reverse scan the significant decrease in the re-reduction peaks indicates the loss of chemical reversibility of the process on the time scale of the experiment after formation of the dication. The CV is reversible if switched back after formation of the monocation (see main text). The two oxidation peaks are assigned to TTF$^{0/+}$ (+0.24 V) and TTF$^{+/2+}$ (+0.49V) respectively. During the first oxidation process, an increase (Figure S5a) in bands at 450 and 595 nm together with a small increase at 786 nm were observed. These bands disappear (Figure S5b) during the second oxidation process. This bleach is consistent with a chemically irreversible process, possible akin to the precipitation observed upon chemical oxidation in the NMR experiment (see main text for details).

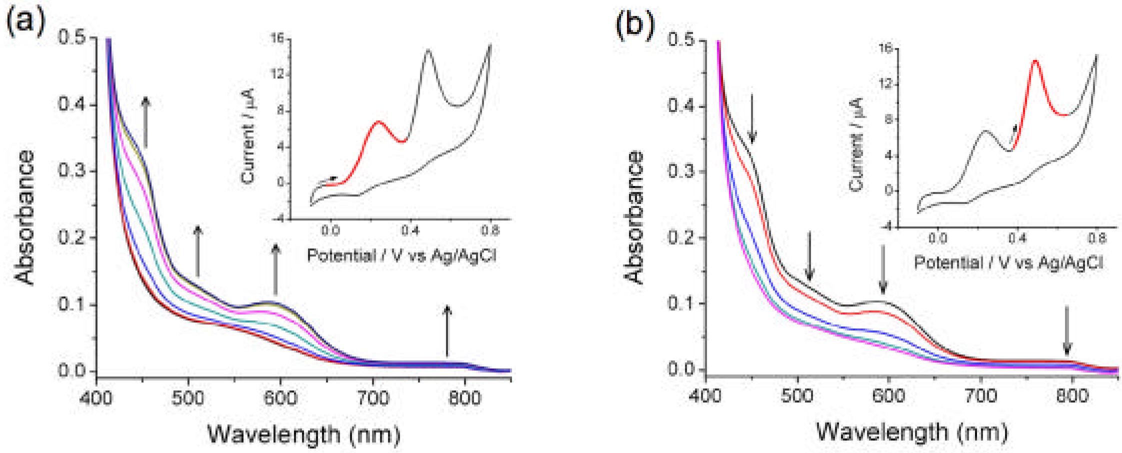

Figure S5: Spectroelectrochemistry of **9**$^{4+}$ through a full forward scan of a CV for the (a) first and (b) second oxidation (0.1 M TBAPF$_6$, 3:1 MeCN:H_2O)

The reversibility of the CV that is switched after the first oxidation (see Figure 6, main text) indicates that the disassembled monocationic TTF^{+} state can be reassembled in the TTF^{0} state. Moreover, the UV-Vis-NIR spectrum recorded at the end of the first CV cycle retains (Figure S6) the same spectroscopic features as the first spectrum before the CV, albeit with some (50%) degradation. Therefore, the monocationic TTF^{+} disassembled state appears more stable than the TTF^{2+}.

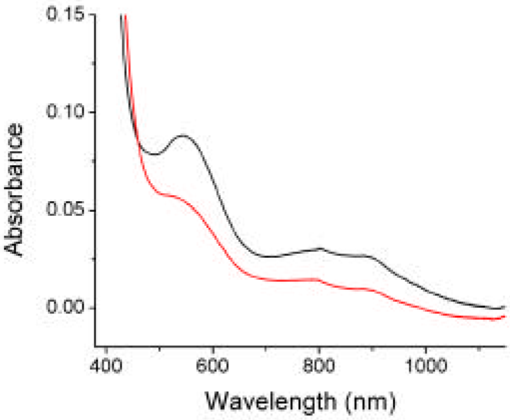

Figure S6: Spectrum of **9**$^{4+}$ recorded in an SEC experiment (corresponding to Figure 6 in the main text) before (black) and after (red) the first oxidation. (0.1 M $TBAPF_6$, 3:1 $MeCN:H_2O$)

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