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Supporting Information

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Gas-Phase Host-Guest Chemistry of Dendritic Viologens with Molecular Tweezers: A Remarkably Strong Dendritic Effect on Dication Stability**

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1. Synthesis of guest viologens

General. Chemicals were purchased from Sigma-Aldrich, Fluka, Merck and used as received. The monomeric branching units **NG1Br** and **NG2Br** were prepared according to literature (G. M. Stewart, M. A. Fox, *J. Am. Chem. Soc.* **1996**, *118*, 4354-4360; M. Plevoets, F. Vögtle, L. De Cola, V. Balzani, *New J. Chem.* **1999**, 63-69). The solvents were dried using standard techniques. Thin-layer chromatography (TLC) was carried out on TLC plates pre-coated with RP-18 F_{254}s (Merck 1.15685). Melting points were determined on a Reichert Thermovar microscope and are not corrected. Mass spectra were recorded using a Concept 1H from Kratos Analytical Ltd., Manchester, GB (FAB), MALDI-TofSpec-E from Micromass, GB (MALDI) and Voyager-DE from PE Biosystems (MALDI). ^{1}H NMR and ^{13}C NMR spectra were recorded using 300 and 400 MHz Bruker instruments.

3^{2+}(PF_6^-)$_2$: A solution of 52.0 mg (0.33 mmol) of 4,4´-bipyridine and 322 mg (0.67 mmol) of **NG1Br** in 20 mL abs. acetonitrile under argon is refluxed for 5d. After cooling to rt, the arising solid is filtered, washed several times with warm acetonitrile and dried. After exchanging counterions to hexafluorophosphate, the product was obtained as an orange solid in 63 % yield (260.2 mg); m.p. 183-186 °C; ^{1}H NMR (400 MHz, [D_6]acetone, 25 °C, TMS): δ = 5.32 (s, 8 H; CH_2), 6.05 (s, 4 H; CH_2), 6.92 (t, ^4J (H,H) = 2 Hz, 2 H; Ar-H), 6.99 (d, ^4J (H,H) = 2 Hz, 4 H; Ar-H), 7.44-7.56 (m, 12 H; Ar-H), 7.82 (m, 12 H; Ar-H), 7.94 (s, 4 H; Ar-H), 8.60 (d, ^3J (H,H) = 7 Hz, 4 H; Py-H), 9.42 (d, ^3J (H,H) = 7 Hz, 4H; Py-H); ^{13}C NMR (100 MHz, [D_6]acetone, 25 °C, TMS): δ = 63.5, 70.1 (CH_2), 102.9, 108.5, 126.3, 126.7, 126.8, 126.9, 127.9, 128.2, 128.3, 128.4, 133.6, 133.9, 134.2, 136.3, 147.2, 149.7, 160.2 (Ar-C); FAB-MS: *m/z* = 962.4 [M-2PF_6]$^+$.

4^{2+}(PF_6^-)$_2$: A solution of 26.0 mg (0.17 mmol) of 4,4´-bipyridine and 349.8 mg (0.35 mmol) of **NG2Br** in 20 mL abs. acetonitrile under argon is refluxed for 5d. After cooling to rt, the

arising solid is filtered, washed several times with warm acetonitrile and dried. After exchanging counterions to hexafluorophosphate, the product was obtained as an orange solid in 62 % yield (242.3 mg); m.p. 127-129 °C; ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 5.05 (s, 8 H; CH$_2$), 5.18 (s, 16 H; CH$_2$), 5.82 (s, 4 H; CH$_2$), 6.70 (t, ^{4}J (H,H) = 2 Hz, 4H; Ar-H), 6.73 (d, ^{4}J (H,H) = 2 Hz, 8 H; Ar-H), 6.75 (t, ^{4}J (H,H) = 2 Hz, 2 H; Ar-H), 6.86 (d, ^{4}J (H,H) = 2 Hz, 4H; Ar-H), 7.40-7.49 (m, 24 H; Ar-H), 7.76-7.86 (m, 32 H; Ar-H), 8.37 (d, ^{3}J (H,H) = 7 Hz, 4 H; Py-H), 9.16 (d, ^{3}J (H,H) = 7 Hz, 4 H; Py-H); ^{13}C-NMR (100 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 63.5, 70.0, 70.1 (CH$_2$), 101.7, 102.8, 108.2, 110.0, 126.4, 126.75, 126.84, 126.9, 127.5, 128.2, 128.3, 128.6, 133.1, 133.3, 135.7, 136.9, 139.5, 146.2, 149.6, 160.0, 160.2 (Ar-C); MALDI-TOF-MS: *m/z* = 2012.1 [M-2PF$_6$]$^{+}$.

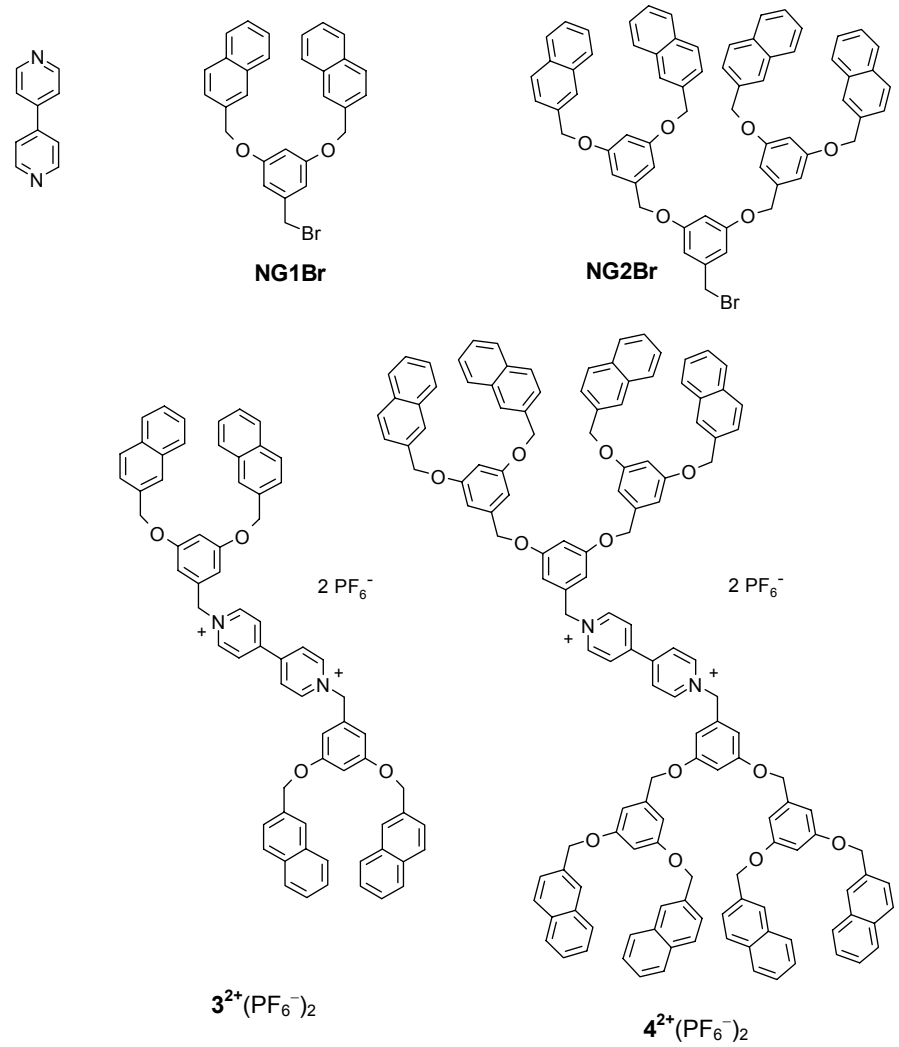

Fig. S1: Starting compounds and viologen dendrimers with 2-naphthyl groups at the periphery.

3. ESI-FT-ICR mass spectrometry

High resolution ESI mass spectra and MS/MS spectra were recorded on a Bruker APEX IV Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source equipped with an off-axis 70^{o} spray needle. Typically, methanol and acetonitrile served as the spray solvent and 30 μM solutions of the analytes were used. Analyte solutions were introduced into the ion source with a syringe pump (Cole-Parmers Instruments, Series 74900) at flow rates of ca. 3 - 4 μL/min. Ion transfer into the first of three differential pumping stages in the ion source occurred through a glass capillary with 0.5 mm inner diameter and nickel coatings at both ends. Ionization parameters - some with a significant effect on signal intensities - were adjusted as follows: capillary voltage: -4.6 to -4.8 kV; endplate voltage: -4.1 to -4.3 kV; capexit voltage: +70 to +90 V; skimmer voltages: +7 to +9 V; temperature of drying gas: 100 ^{o}C. The flows of the drying and nebulizer gases were kept in a medium range (ca. 10 psi). The ions were accumulated in the instruments hexapole for 2 - 3 s, introduced into the FT-ICR cell, which was operated at pressures below 10^{-10} mbar and detected by a standard excitation and detection sequence. For each measurement 16 to 256 scans were averaged to improve the signal-to-noise ratio.

For MS/MS experiments, the whole isotope patterns of the ion of interest were isolated by applying correlated sweeps, followed by shots to remove the higher isotopes. After isolation, argon was introduced into the ICR cell as the collision gas through a pulsed valve at a pressure of ca. 10^{-8} mbar. The ions were accelerated by a standard excitation protocol and detected after a 2 s pumping delay. A sequence of several different spectra was recorded at different excitation pulse attenuations in order to get at least a rough and qualitative idea of the effects of different collision energies on the fragmentation patterns. During the double resonance experiment, the CID experiment was repeated under the exact same conditions. The intermediate to be examined for consecutive fragmentations was ejected from the ICR cell during the whole duration of the experiment by a high frequency pulse.