

## Supporting Information

### Synthesis and Linear and Nonlinear Absorption Properties of Dendronised Ruthenium(II) Phthalocyanine and Naphthalocyanine

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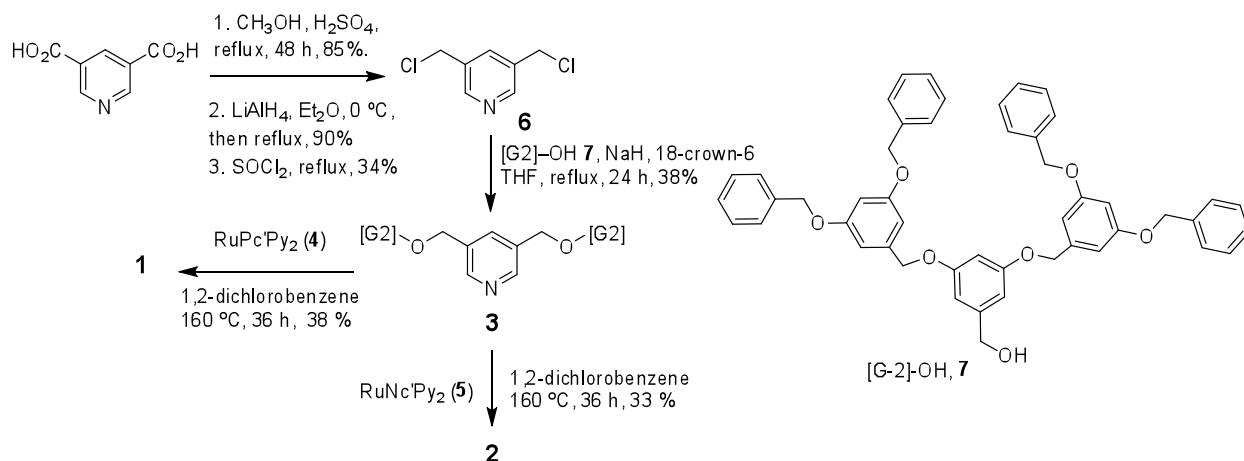
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**General:** All chemicals were purchased from commercial sources and used as received, unless stated otherwise. 3,5-Di(chloromethyl)pyridine (**6**)<sup>1</sup>, G2-OH (**7**)<sup>2</sup> and **4**<sup>3</sup> were synthesised according to literature procedures. 6-(*tert*-butyl)naphthalene-2,3-dicarbonitrile was obtained from commercial sources and **5**<sup>4,5</sup> was synthesised according to a modification of a literature procedure. Column chromatography was carried out using silica-gel (46-63  $\mu\text{m}$ , Sorbent) as the stationary phase, and thin-layer chromatography (TLC) was performed on precoated silica-gel plates (0.25 mm thick, 60F254, EMD, Germany) and visualised under UV light. Preparative TLC was performed on 20  $\times$  20 cm glass plates coated with 1.0 mm thick silica-gel (EMD, Germany).

The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were measured on a Varian Mercury 300 MHz and 400 MHz spectrometers in  $\text{CDCl}_3$ . The chemical shift values are expressed as  $\delta$  values and were referenced with the solvent residual  $\text{CHCl}_3$  signal as internal standard. Mass spectra were measured on an Applied Biosystems 4700 Proteomics Analyzer using MALDI mode. Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer.

UV-vis-NIR absorption spectra were recorded on a Varian Cary 500 spectrophotometer. Quartz cuvettes with 1 cm, 1mm, and 50  $\mu\text{m}$  path lengths were employed to collect data for solutions with concentrations of ca.  $10^{-6}$ ,  $10^{-4}$  and  $10^{-3}$  M concentration, respectively. For the measurements of thin film absorption spectra, solutions were spin-coated at 1000 rpm for 1 min onto pre-cleaned glass slides from 12 mg/mL solutions in chlorobenzene. Thick films for optical-limiting measurements were obtained by spin-coating at 500 rpm for 4 min from cyclohexanone solutions; thicknesses were measured used profilometry. Optical-limiting measurements were performed by exciting the sample with 6 ns pulses of 475 and 500 nm light focused in an f/5 geometry down to a 20  $\mu\text{m}$  spot, and monitoring the change in transmittance as a function of pulse energy. The laser pulses at both wavelengths were produced using an optical parametric oscillator (Newport Spectra-Physics) pumped by the third harmonic of an Nd:YAG laser (Newport Spectra-Physics). Part of the excitation beam before the sample was deflected to a reference photodetector, so that changes in the signal transmitted through the sample could be compared to the intensity of the incident beam. The signal and reference were detected on New Focus photoreceivers (San Jose, California), and their responses were integrated using a Stanford Research Systems boxcar averager (Sunnyvale, CA). Deaerated solutions were prepared in 1 cm cuvettes with transmittances of 0.7. In all cases, the focus of the excitation was approximately half-way through the sample.



**Scheme 1.** Synthesis of dendrimers.

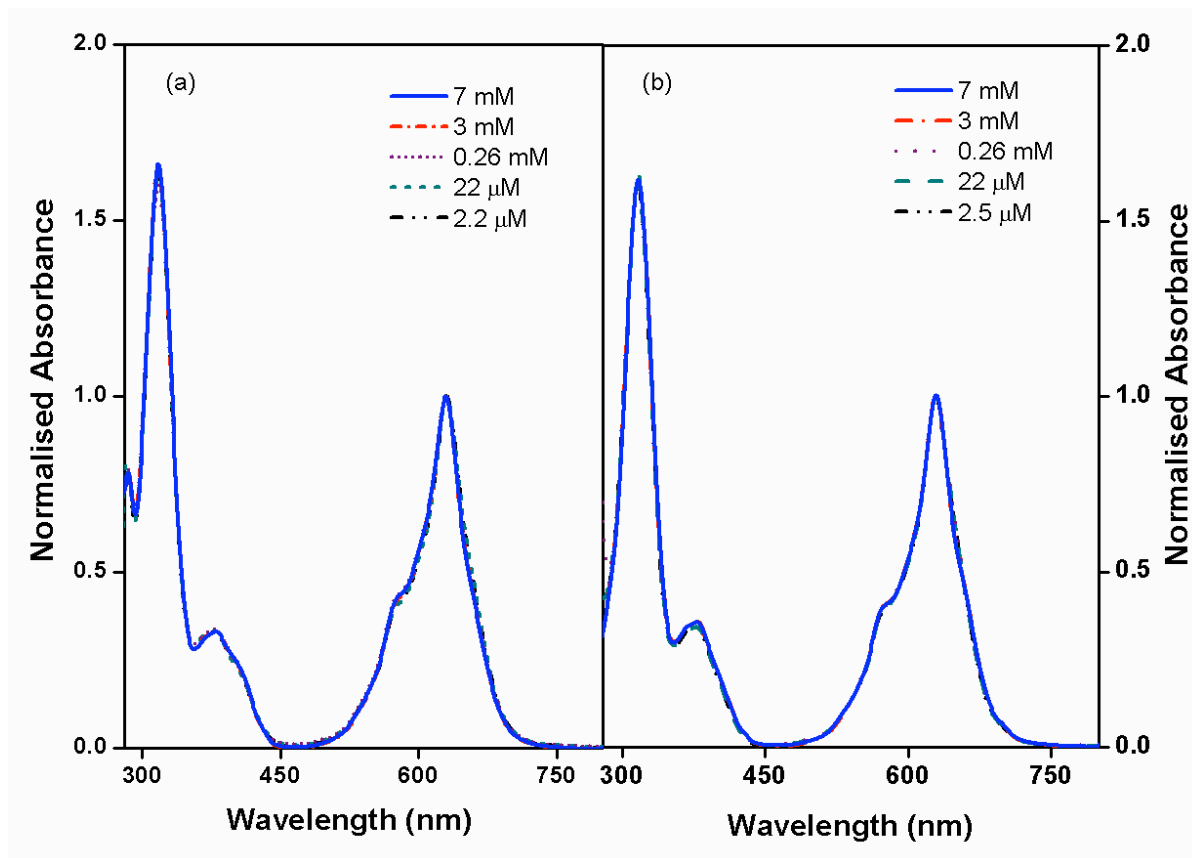
**3.** The Fréchet-type G2 dendronised alcohol, **7** (17.0 g, 22.8 mmol), was added to a solution of NaH (0.86 g, 36 mmol) in dry THF (100 mL) under  $\text{N}_2$ . The reaction mixture was stirred at room temperature for 15 min, after which a mixture of 18-crown-6 (1.52 g, 1.70 mmol) and 3,5-di(chloromethyl)pyridine (1.6 g, 9.1 mmol) in dry THF (50 mL) was added dropwise. The reaction mixture was heated to reflux for 24 h. Upon completion, the product was extracted with ethyl acetate. The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated under reduced pressure. The crude product was purified by column chromatography (silica-gel, 60% v/v ethyl acetate in hexanes) to yield a colorless oil (5.4 g, 38%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.50 (d,  $J = 1.8$  Hz, 2H), 7.70 (s, br, 1H), 7.34 (m, 40H), 6.59 (m, 18H), 4.98 (s, 16H), 4.92 (s, 8H), 4.51 (s, 4H), 4.48 (s, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  159.9, 159.8, 148.2, 140.1, 139.1, 136.7, 134.6, 133.3, 128.5, 127.9, 127.5, 106.6, 106.3, 101.5, 101.4, 72.5, 70.0,

69.8, 69.3. MALDI-TOF/MS:  $m/z$  1592 ( $M^+$ ). Anal Calcd. For  $C_{105}H_{93}NO_{14}$ : C, 79.17; H, 5.88; N, 0.88, O, 14.06. Found C, 79.09; H, 6.06; N, 0.83; O, 14.35.

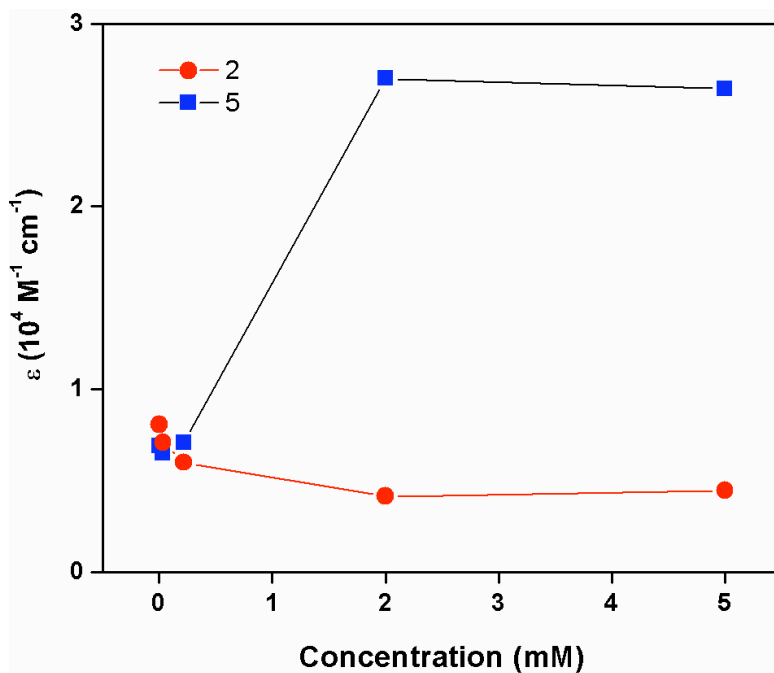
**1.** A mixture of **4** (0.20 g, 0.20 mmol), **3** (1.30 g, 0.82 mmol) and 1,2-dichlorobenzene (12 mL) was heated at 160 °C for 36 h. The reaction mixture cooled to room temperature, and the solvent was evaporated under reduced pressure. The crude product was passed through a silica-gel plug (90:10 v/v toluene: ethyl acetate) to afford a blue solid, which was further subjected to size-exclusion chromatography (THF) followed by preparative thin-layer chromatography (95:5 v/v toluene / ethyl acetate) to give **1** as a blue solid. Yield: 0.32 g (38%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  9.10 (m, 4H), 9.05 (m, 4H), 7.80 (m, 4H), 7.28 (m, 80H), 6.56 (s, 16H), 6.47 (s, 8H), 6.31 (s, 4H), 6.07 (s, 8H), 6.00 (s, br, 2H), 4.92 (m, 32H), 4.74 (s, 16H), 3.43 (s, 8H), 3.03 (s, 8H), 2.35 (m, 4H), 1.59 (m, 36H). MALDI-TOF/MS  $m/z$  4023 ( $M^+$ ). Anal Calcd. For  $C_{258}H_{234}N_{10}O_{28}Ru$ : C, 77.01; H, 5.86; N, 3.48; O, 11.13, Found: C, 77.23; H, 6.06; N, 3.62.

**2.** A mixture of **5** (0.20 g, 0.16 mmol), **3** (1.10 g, 0.75 mmol) and 1,2-dichlorobenzene (10 mL) was heated at 160 °C for 36 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The crude product was passed through a silica-gel plug (90:10 v/v toluene / ethyl acetate) to afford a green solid, which was further subjected to a size-exclusion chromatography (THF) followed by preparative thin-layer chromatography (95:5 v/v toluene: ethyl acetate) to give **2** as a green solid. Yield: 0.25 g (33 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  9.66 (s, br, 4H), 9.62 (s, br, 4H), 8.27 (m, 8H), 7.74 (m, 4H), 7.37-7.23 (m, 80H), 6.53 (s, 16 H), 6.45 (s, 8H), 6.28 (s, 4H), 6.02 (s, 10H), 4.88 (s, 32 H), 4.66 (s, 16H), 3.53 (s, 8H), 3.02 (s, 8H), 2.69 (s, 4H), 1.59-1.44 (m, 36 H). MALDI-TOF/MS:  $m/z$  4223; found 4224 ( $M+H^+$ ). Anal Calcd. For  $C_{274}H_{242}N_{10}O_{28}Ru$ : C, 77.91; H, 5.77; N, 3.32; O, 10.61, Found: C, 77.74; H, 5.90; N, 3.27.

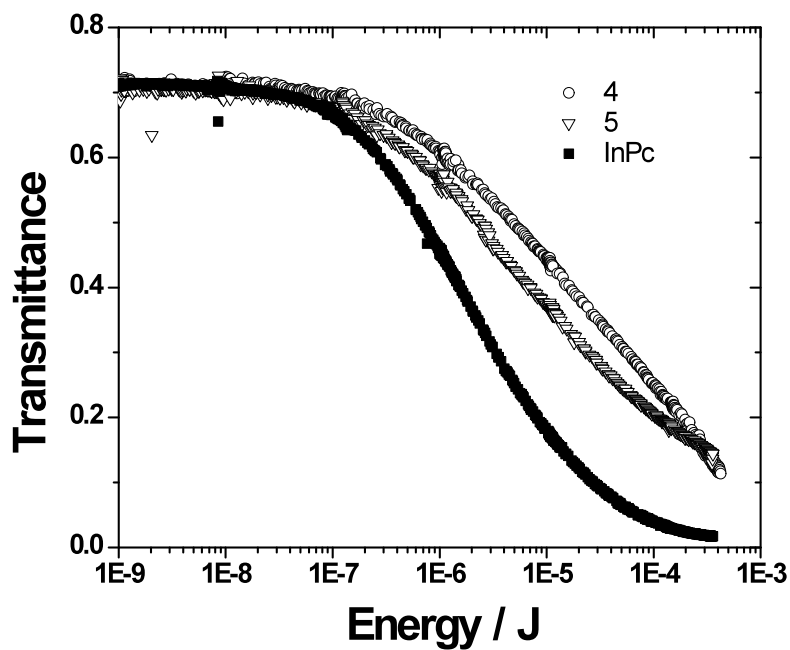
**5.** To a stirred solution of 6-(*tert*-butyl)naphthalene-2,3-dicarbonitrile (2.9 g, 12.4 mmol),  $RuCl_3 \cdot xH_2O$  (0.81 g, 3.1 mmol) and 2-ethoxyethanol (15 mL) under  $N_2$  was added 1,8-diazabicyclo[5.4.0]undec-7-ene (1 mL) and pyridine (2.5 mL, 50 mmol). The reaction was heated to reflux for 24 h. Upon completion, mixture poured in 1:1  $H_2O$  / MeOH mixture. The resulting precipitate was collected by filtration and was washed with water, methanol, and acetone. The crude product was purified by column chromatography (silica-gel, chloroform) to yield a green solid (1.4 g, 30 %). Characterization data was in agreement with the literature.<sup>5</sup>



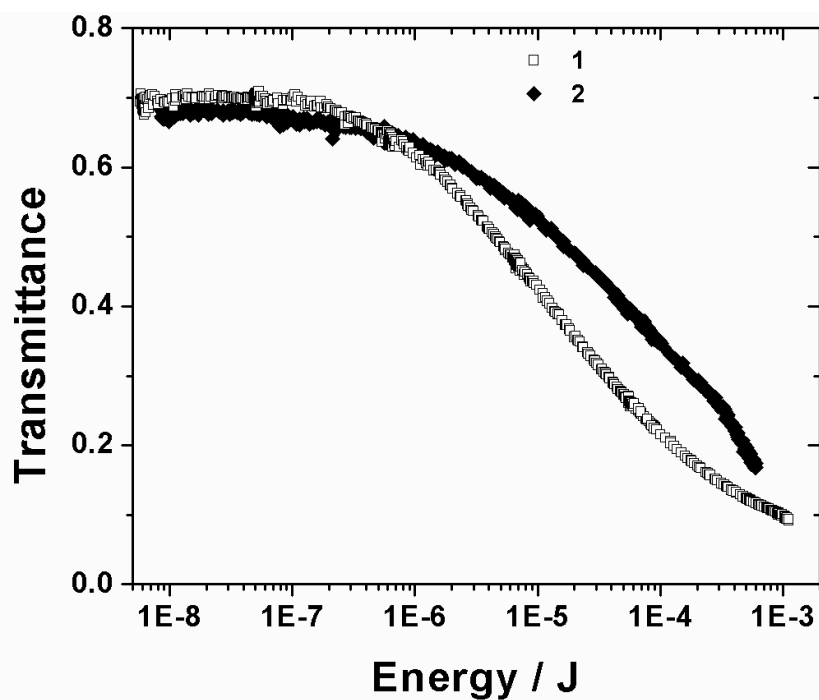
**Figure S1.** (a) Variable concentration UV-vis-NIR absorption spectra of **1** and (b) **4** in toluene solution (2.2 μM – 7 mM).



**Figure S2.** Plot of absorptivity vs. concentration for RuNc' derivatives at 750 nm.



**Figure S3.** Optical-limiting of 4 (230  $\mu\text{M}$ ), 5 (35  $\mu\text{M}$ ), and InPc'Cl (660  $\mu\text{M}$ ) in toluene. The sample was excited using 475 nm, 6 ns pulses focused in an  $f/5$  geometry into the middle of a 1 cm pathlength cell.



**Figure S4.** Optical-limiting of 1 (94  $\mu\text{M}$ ) and 2 (65  $\mu\text{M}$ ) in toluene at 500 nm.

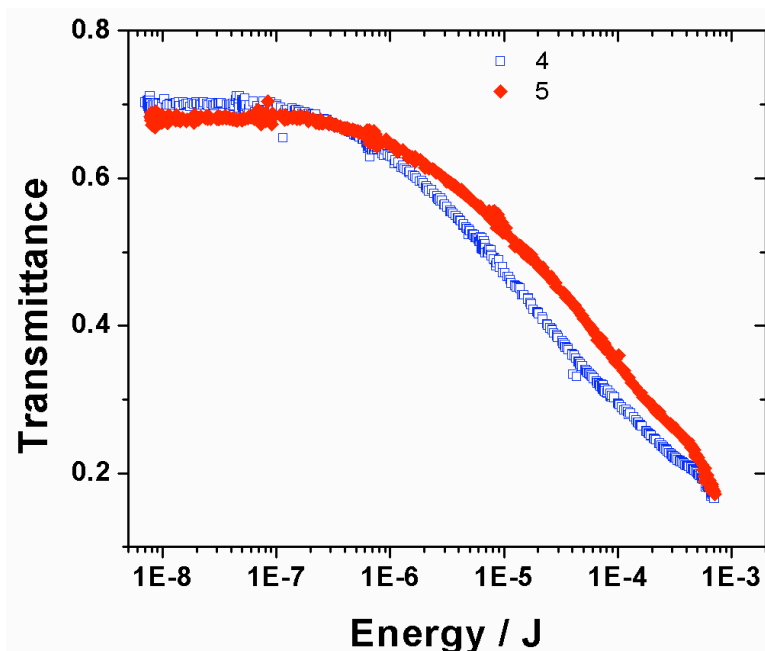


Figure S5. Optical-limiting of 4 (89  $\mu\text{M}$ ) and 5 (76  $\mu\text{M}$ ) in toluene at 500 nm.

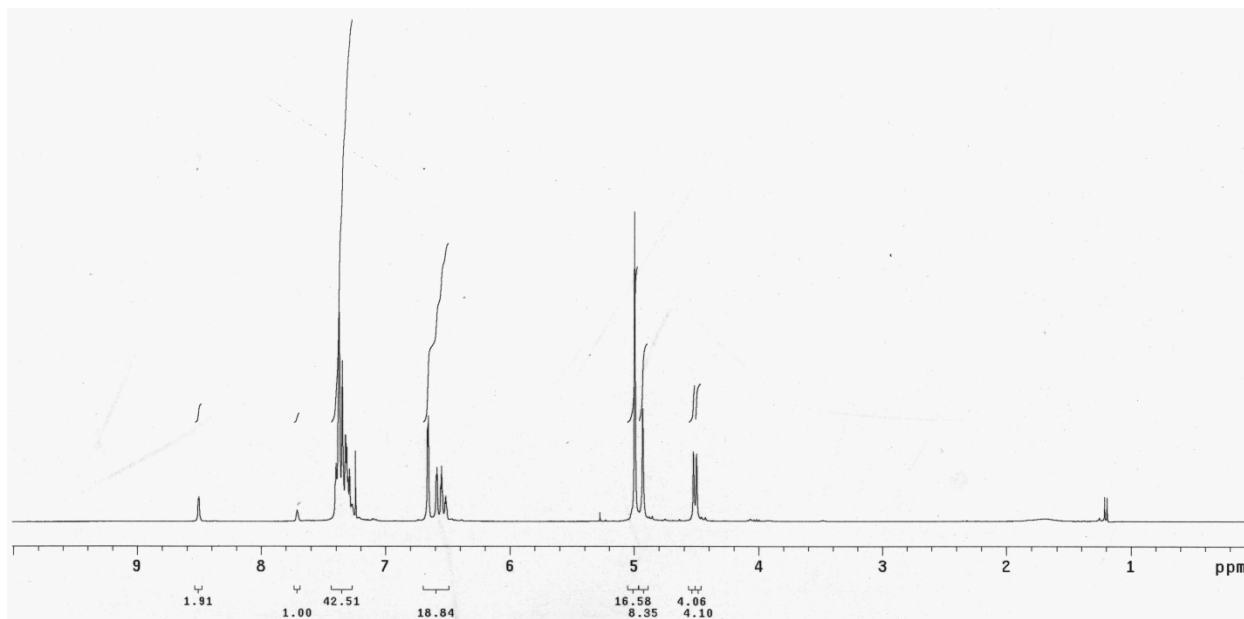
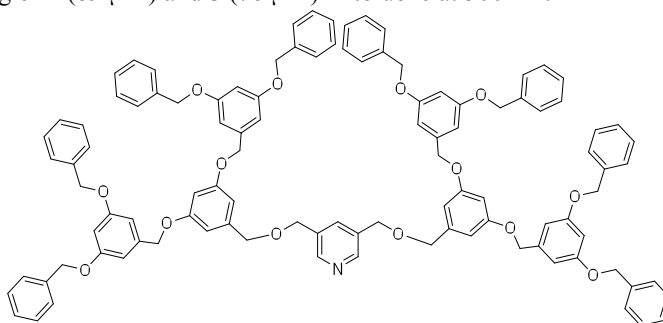
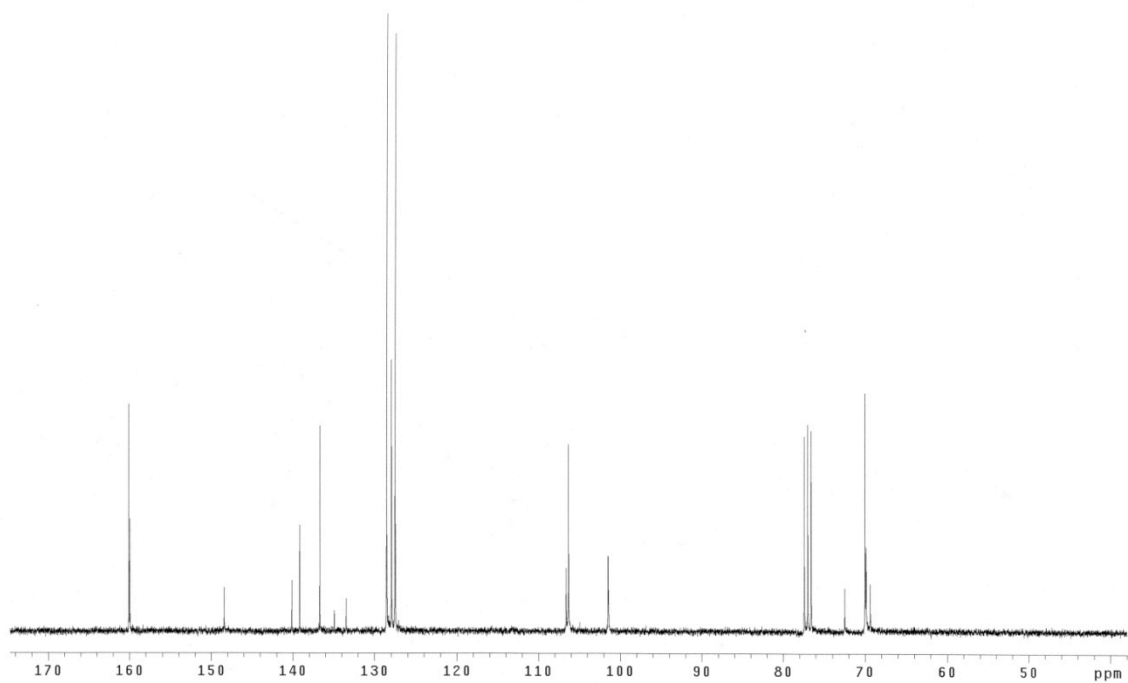


Figure S6.  $^1\text{H}$  NMR spectrum of 3 in  $\text{CDCl}_3$ .



**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .

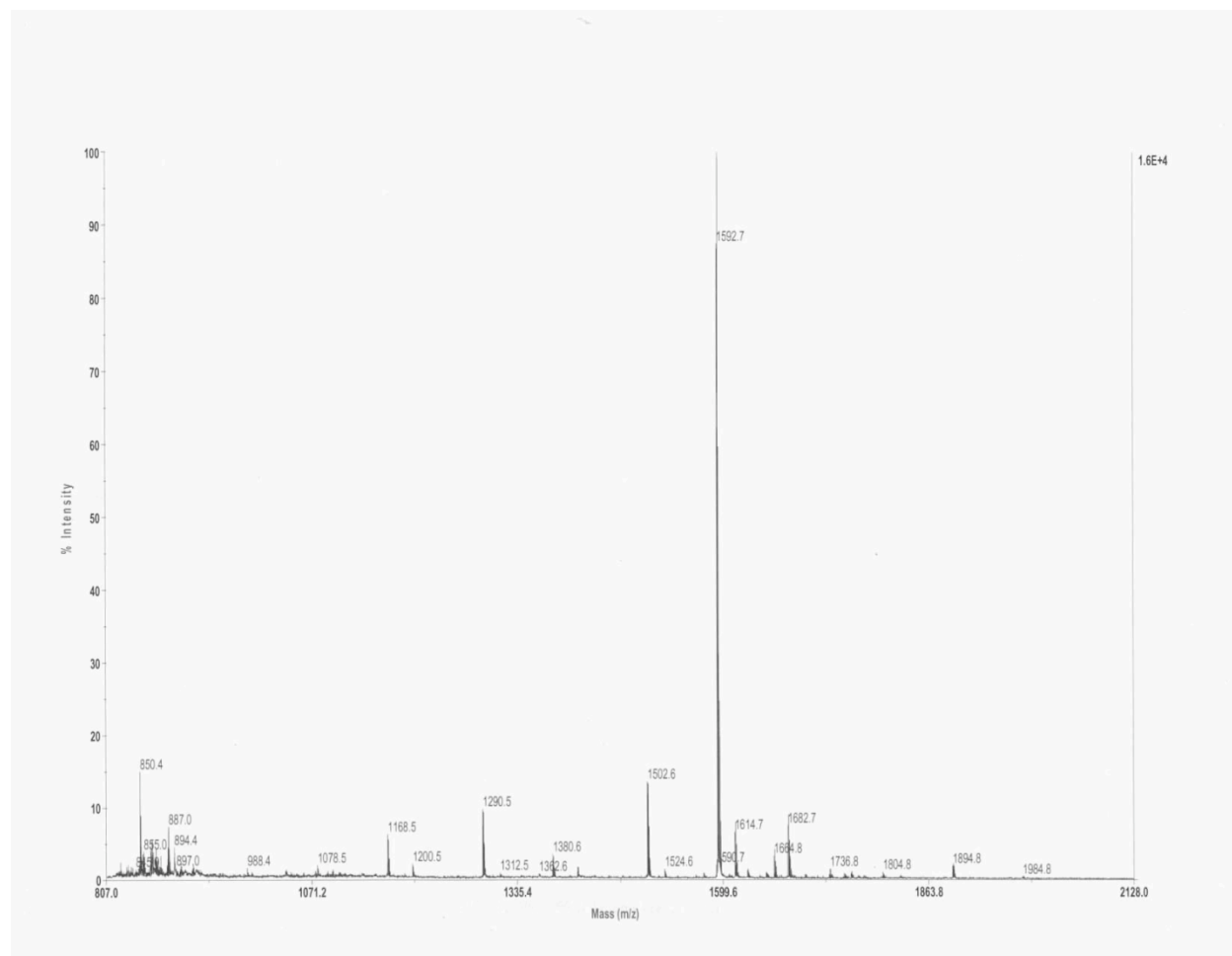


Figure S8. MALDI spectrum of 3.

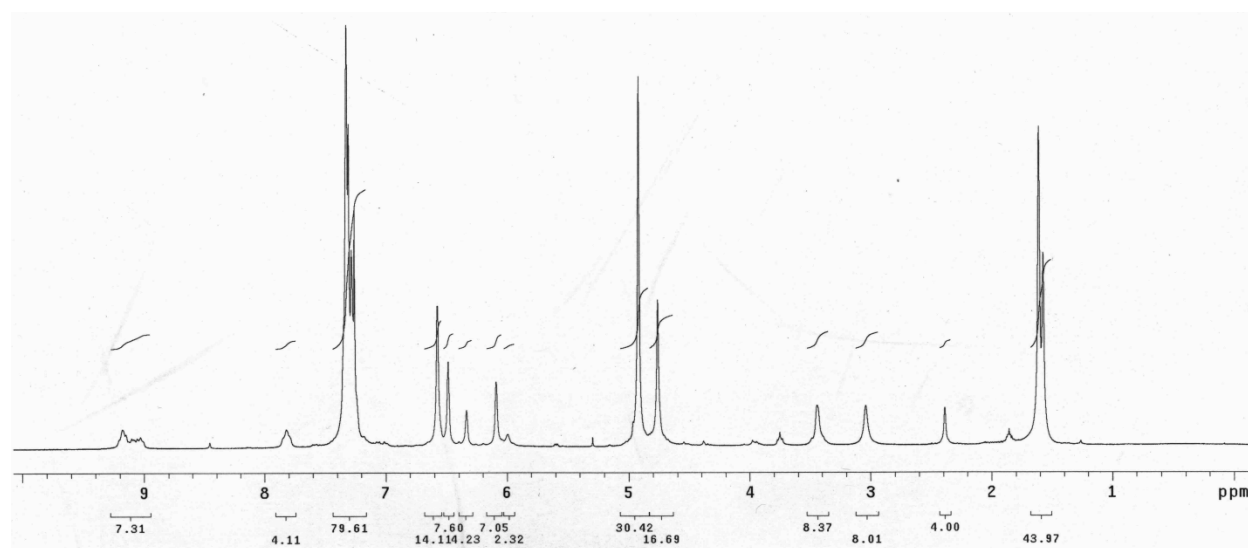
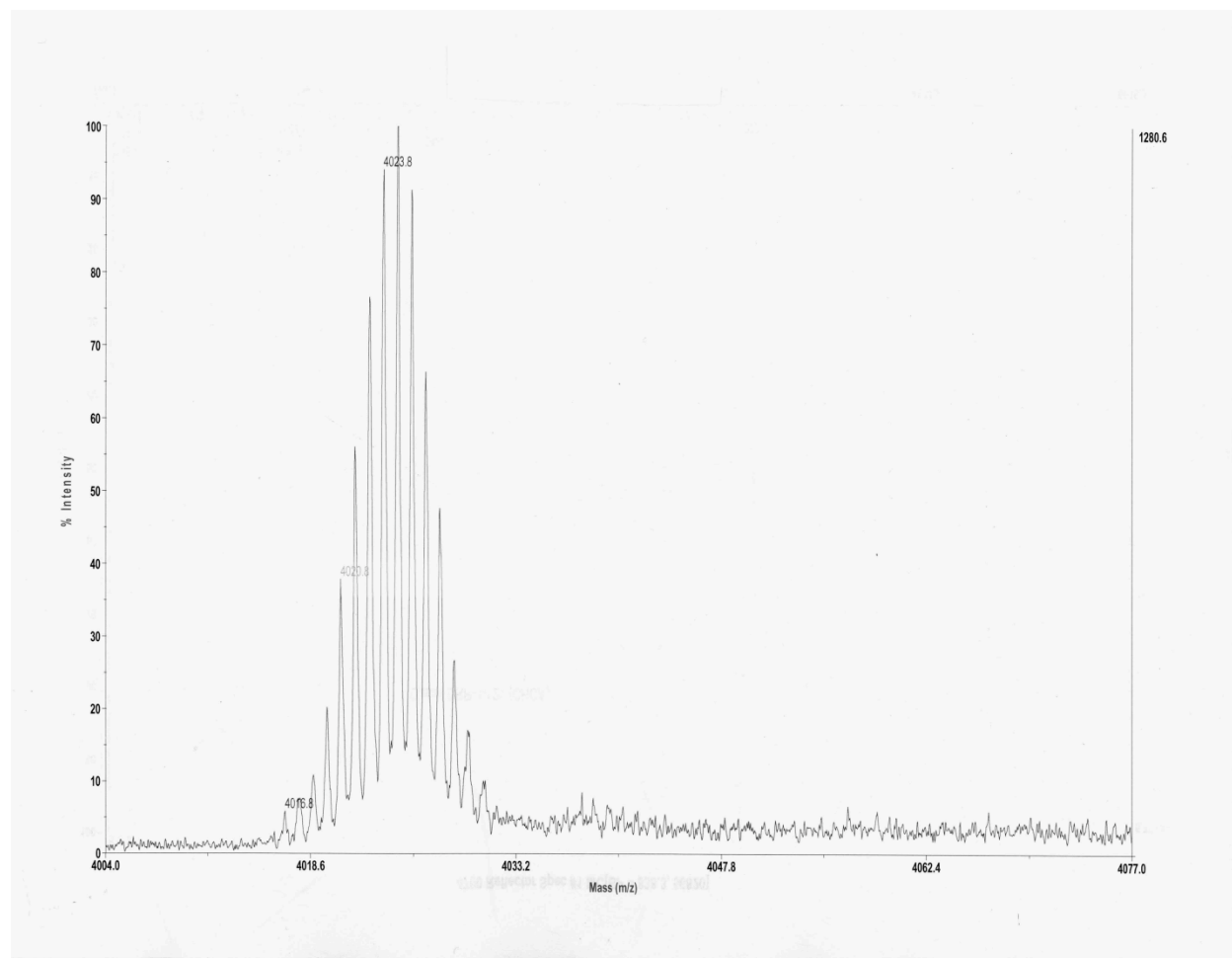
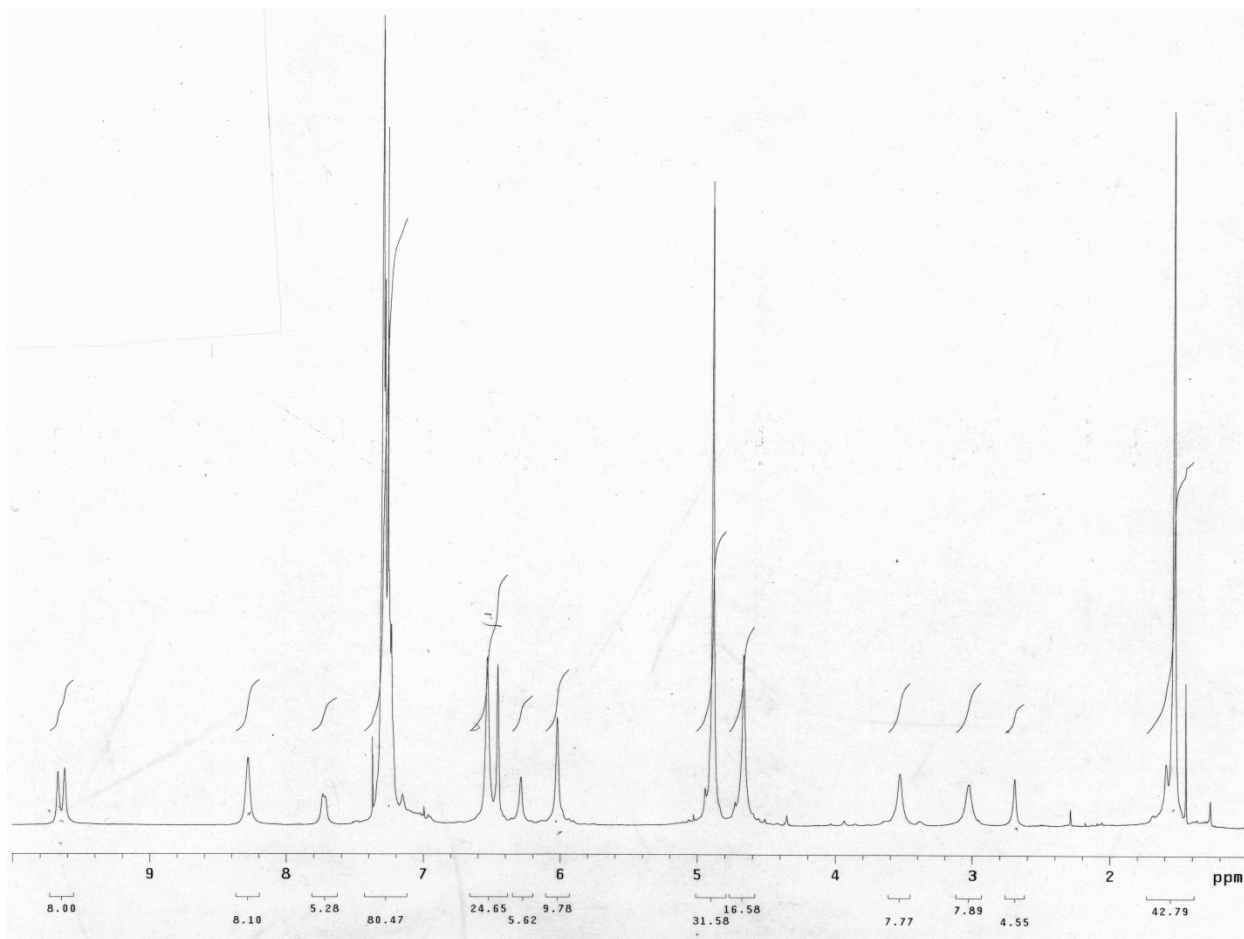


Figure S9. <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3</sub>.

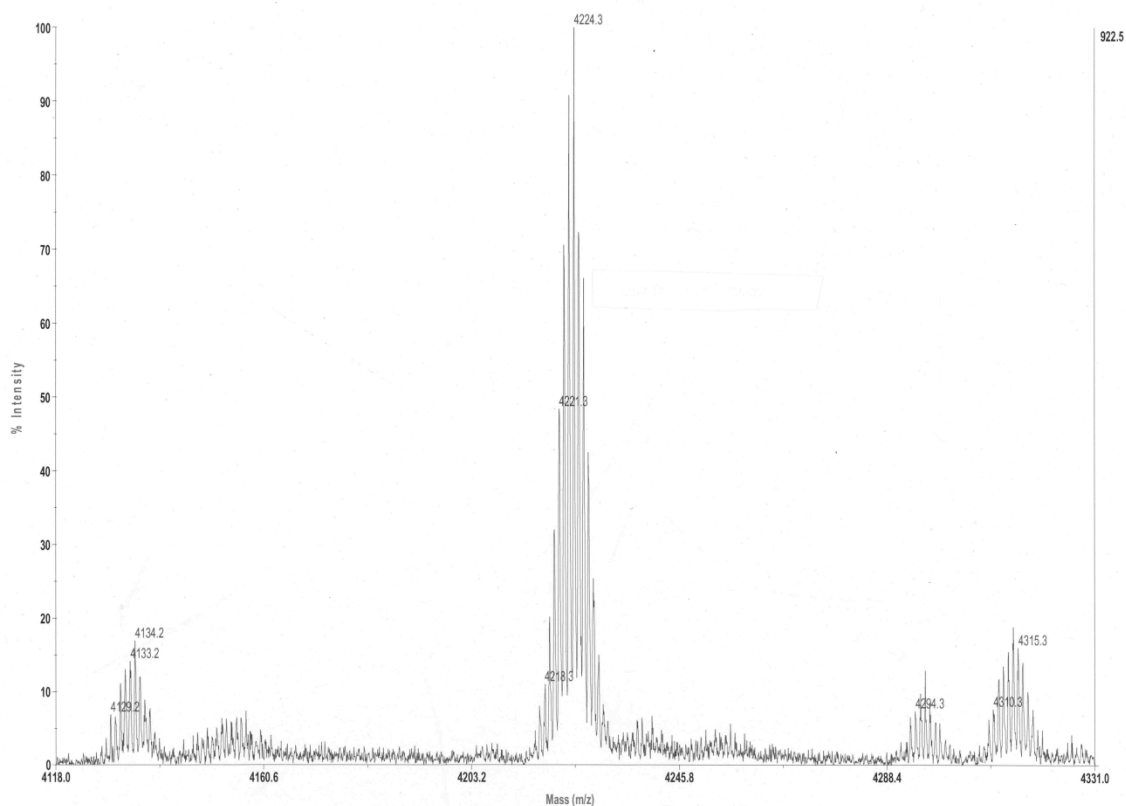




**Figure S10.** MALDI spectrum of **1**.



**Figure S11.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .



**Figure S12.** MALDI spectrum of **2**.

## References

1. M.-C. Lagunas, R.-A. Gossage, W. J. J. Smeets, A. L. Spek and G. van Koten. *Eur. J. Inorg. Chem.* **1998**, 163.
2. C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638.
3. M. Hanack and P. Vermehren, *Chem. Ber.*, **1991**, *124*, 1733.
4. M. Hanack, S. Knecht and R. Polley, *Chem. Ber.*, **1995**, *125*, 929.
5. K. Ishii, M. Shiine, Y. Shimizu, S.-i. Hoshino, H. Abe, K. Sogawa and N. Kobayashi, *J. Phys. Chem. B* **2008**, *112*, 3138.