

Supporting Material

The Perchloro-2,5,8-triazaphenalenyl Radical

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General remarks. All reactions were performed under argon. All NMR studies were carried out on Bruker ARX-500 or ARX-400 spectrometers. Me₄Si was used as the internal standard for ¹H NMR and the deuterated solvent was used as a standard for ¹³C NMR. The matrix used for FAB mass spectra was *m*-nitrobenzyl alcohol; FT-IR spectra were recorded on a Perkin-Elmer Paragon-1000 instrument. ESR spectra were recorded on a Bruker ESP380E spectrometer. Column chromatography was performed on silica gel 230-400 mesh (flash) from E. Merck or from Scientific Absorbents; thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F₂₅₄ from E. Merck. Cyclic voltammetry was carried out using Bioanalytical System CV-50W voltammetric analyzer.

Synthesis:

Diethyl 4-oxo-1,4-dihydro-3,5-pyridinedicarboxylate (4): A mixture of diethyl 1,3-acetonedicarboxylate (20 mL, 0.1 mol), triethyl orthoformate (30 mL, 0.2 mol) and urea (9.0 g, 0.15 mol) in 50 mL of xylenes was heated to reflux for 3 h. After all the urea was dissolved and light yellow precipitate formed, the formed ethanol was distilled out (about 55 mL), then the mixture refluxed for an additional 20 minutes. After cooling, the suspension was filtered and washed with xylenes (2 x 20 mL) and methylene chloride (2 x 30 mL), dried under vacuum to give compound **4** as a light yellow solid (22 g, 92%).

m.p. 240 °C (subl). ^1H NMR (500 MHz, DMSO) δ 1.25 (t, J = 7.3 Hz, 6H), 4.19 (q, J = 7.3 Hz, 4H), 8.18 (s, 2H), 11.16 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 14.5, 60.6, 121.8, 142.5, 147.8, 164.8. IR (KBr) 3428, 2986, 1702, 1644, 1602, 1528, 1375, 1354, 1280, 1238, 1164, 1106, 1027, 911, 816, 606. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_5$ (M+H) 239.0794, found 239.0793.

Diethyl 4-chloro-3,5-pyridinedicarboxylate (5): A mixture of compound **4** (1.3 g, 5.5 mmol) and phosphorous oxychloride (6 mL) in a sealed tube was heated at 140 °C for 12 h. After cooling down, the solution was carefully poured into ice. The aqueous mixture was extracted with ice-cold ether (3 x 100 mL). The organic layer was washed with ice water (3 x 100 mL), then dried with anhydrous magnesium sulfate, concentrated to 10 mL and passed through a pad of silica gel (ethyl acetate). Evaporation of the solvent gave compound **5** as a colorless oil (0.73 g, 52%). ^1H NMR (500 MHz, CDCl_3) δ 1.43 (t, J = 7.1 Hz, 6H), 4.46 (q, J = 7.1 Hz, 4H), 8.98 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 62.4, 128.2, 142.7, 152.9, 163.7. IR (CCl_4): 2985, 1740, 1569, 1278, 1194, 1024. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{12}\text{ClNO}_4$ 257.0455, found 257.0449.

Compound 6: To a suspension of potassium hydride (0.80 g, 20 mmol) in 20 mL of dry diethyl ether was added malononitrile (1.32 g, 20 mmol). The mixture was stirred for 2 h at room temperature, then compound **5** (2.0 g, 4.4 mmol) was added. The whole suspension was heated to reflux at 40 °C for 2.5 h. After cooling, the reaction was quenched with a mixture of saturated aqueous ammonium chloride and 2N HCl (2:1). The aqueous solution was extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate, concentrated and purified by column chromatography (SiO_2 , ethyl acetate). The collected fractions containing **6** were concentrated to 10 mL and cooled down to give pure material as a yellow crystalline solid (1.2 g, 50%). m.p. 220-222 °C. ^1H NMR (500 MHz, CD_3OD) δ 1.37 (t, J = 7.2 Hz, 6H), 4.36 (q, J = 7.2 Hz,

4H) 8.00 (s, 2H). ^{13}C NMR (125 MHz, DMSO) δ 14.28, 63.02, 118.01, 119.11, 139.68, 151.68, 166.41. IR (KBr): 3317, 3104, 2984, 2205, 2183, 1725, 1710, 1643, 1561, 1513, 1470, 1393, 1366, 1298, 1213, 1169, 1144, 1116, 1106, 1016, 864, 148, 734, 586. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4$ 287.0906, found 287.0908.

1,1,3,4,6,7,9-Heptachloro-2,5,8-triazaphenalene (3): A mixture of compound **6** (100 mg, 0.34 mmol), PCl_5 (940 mg, 3.4 mmol) and $\text{Me}_4\text{N}^+\text{Cl}^-$ (160 mg, 1.4 mmol) was ground to a powder in a moisture-protected screw-cap sealed tube. The whole mixture was heated at 150°C for 6 h. The resulting solid was dissolved in ethyl acetate (20 mL) and poured into ice. After quickly extracting the aqueous layer with ethyl acetate only once (20 mL), the organic layer was dried with anhydrous magnesium sulfate, and passed as quickly as possible through a pad of silica gel (ethyl acetate). Evaporation of the solvent under vacuum gave unavoidable mixtures of compound **3** and imide **7** as a red viscous oil (90 mg). A 4:1 mixture of compounds **3** and **7** was characterized by ^{13}C NMR and mass spectrometry where compound **3** has the following data: ^{13}C NMR (100 MHz, CDCl_3) δ 92.0, 110.8, 116.3, 122.4, 140.5, 149.4, 149.9, 151.6, 152.7, 153.6. IR (KBr): 1560, 1541, 1146. HRMS (EI) calcd for $(\text{M}-\text{Cl})^+$ 371.8223, found 371.8210.

Compound 7: Single crystals of compound **7** were also obtained during an attempted recrystallization of radical **1** with CH_2Cl_2 /hexane in the presence of air. m.p. $> 250^\circ\text{C}$. ^{13}C NMR (100 MHz, CDCl_3) δ 112.4, 117.5, 145.4, 154.3, 155.3, 158.5. MS (EI): calcd $\text{C}_{10}\text{HCl}_4\text{N}_3\text{O}_2$ 334.8823, found 334.9. UV-vis (CH_2Cl_2) λ (nm) 233 ($\epsilon = 110,000$), 255 (121,000), 282 (101,000), 417 (57,300), 697 (4020). IR (KBr): 3288, 1716, 1693, 1557, 1541, 1292, 1219, 1149, 1091, 955, 820, 754. X-ray structure shown in Figure S-3.

Perchloro-2,5,8-triazaphenalenyl radical (1): To a solution of compound **3** (90 mg, 0.22 mmol) in 10 mL of CH_2Cl_2 was slowly added a solution of tetramethylammonium iodide in CH_2Cl_2 (80 mg, 0.22 mmol). The mixture turned deep blue within 2 minutes. To the solution was added 5 mL of hexane and the solution was immediately submitted to column chromatography (SiO_2 , CH_2Cl_2 /hexane 2:1) to separate the deep blue radical **1**

from small amounts of deep blue dimer **2** and other colored impurities. After evaporation of the solvent under vacuum, compound **1** was obtained as a dark blue solid (10 mg, 12%). Radical **1** was characterized by ESR spectroscopy and HRMS. HRMS (EI): calcd for $C_{10}C_{16}N_3$ 371.8223, found: 371.8217. UV-vis (CH_2Cl_2) λ (nm) 228 ($\epsilon = 13,000$), 381 (11,100), 622 (1,590). Anal. calcd for $C_{10}Cl_6N_3$: C, 32.04; Cl, 56.75; N, 11.21; Found C, 32.74; Cl, 55.97; N, 10.69.

π -Bonded dimer 2: To a solution of compound **3** (90 mg, 0.22 mmol) in 10 mL of CH_2Cl_2 was slowly added a solution of two equivalents of tetramethylammonium iodide (200 mg, 0.55 mmol). The mixture turned to deep blue within 2 minutes. To the resulting mixture was added 5 mL of hexanes and the solution was submitted quickly to column chromatography (SiO_2 , CH_2Cl_2 /hexanes 2:1). After evaporation of the collected fraction under vacuum, compound **2** was obtained as a red brown crystalline solid (22 mg, 26%). Reddish single crystals were obtained by slow diffusion of hexane into a solution of compound **2** in CH_2Cl_2 under argon. m.p. > 300 °C. No signal was observed by ^{13}C NMR spectrometry, likely due to radical impurities present in the sample. IR (KBr): 1560, 1261, 1184, 803, 661. UV-vis (CH_2Cl_2): λ (nm) 239 ($\epsilon = 17,600$), 326 (11,400), 685 (12,700). MALDI-MS: 673.7 (M^+), 638.8 ($M-Cl$), 603.8 ($M-2Cl$).

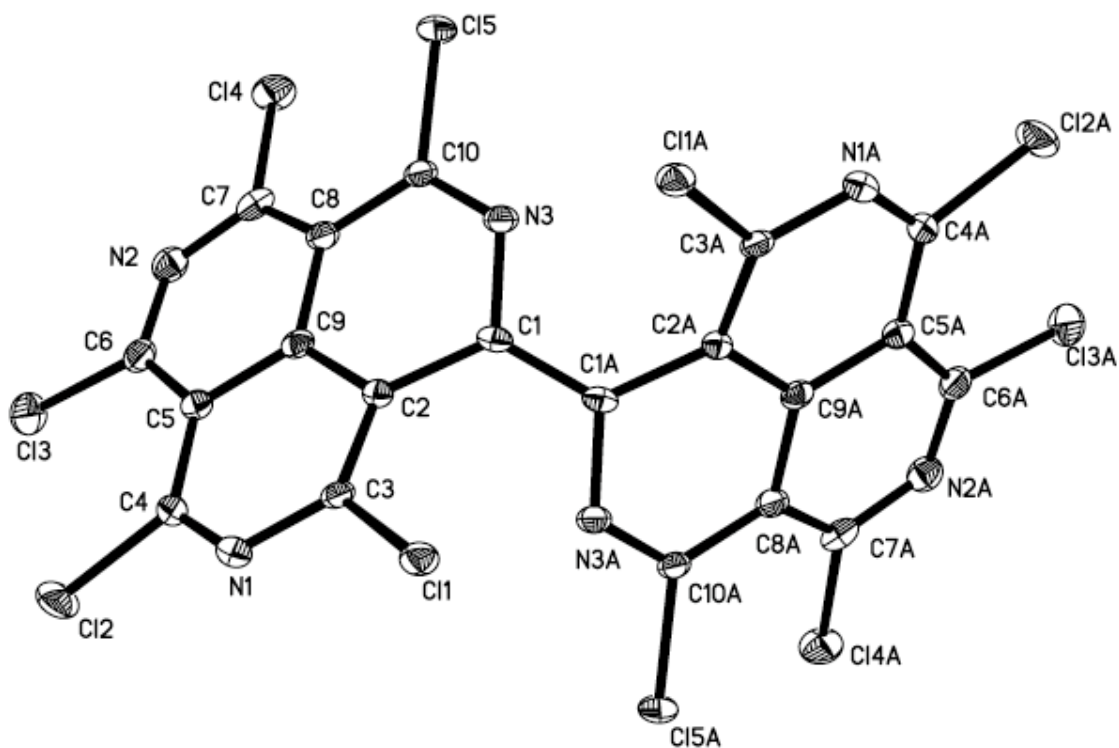


Figure S-1. X-ray structure of the perchloro-2,5,8-triazaphenalenyl π -bonded dimer (**2**).

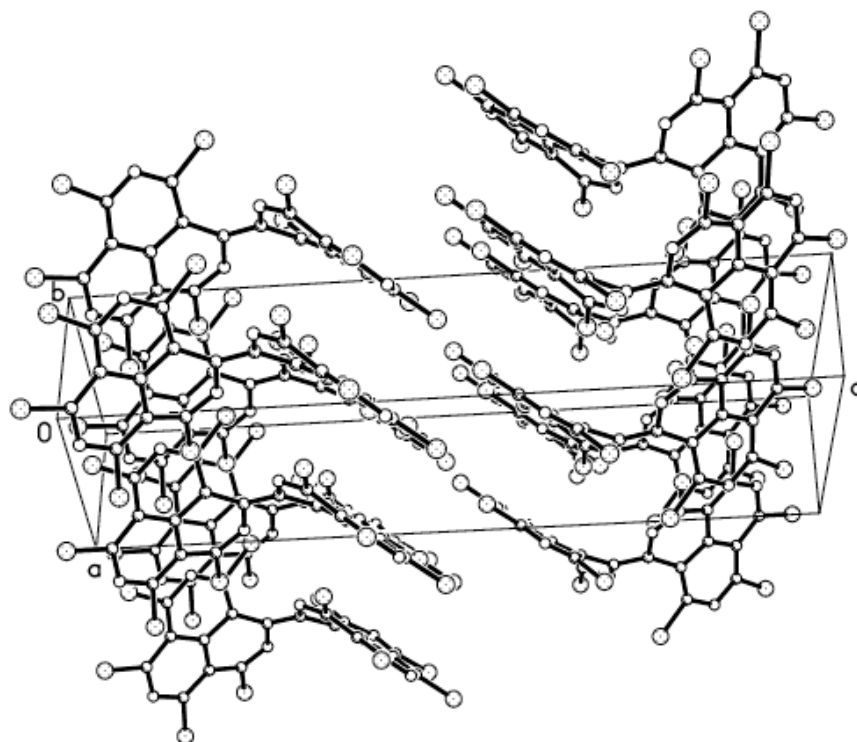


Figure S-2. Cell packing of the perchloro-2,5,8-triazaphenalenyl dimer (**2**).

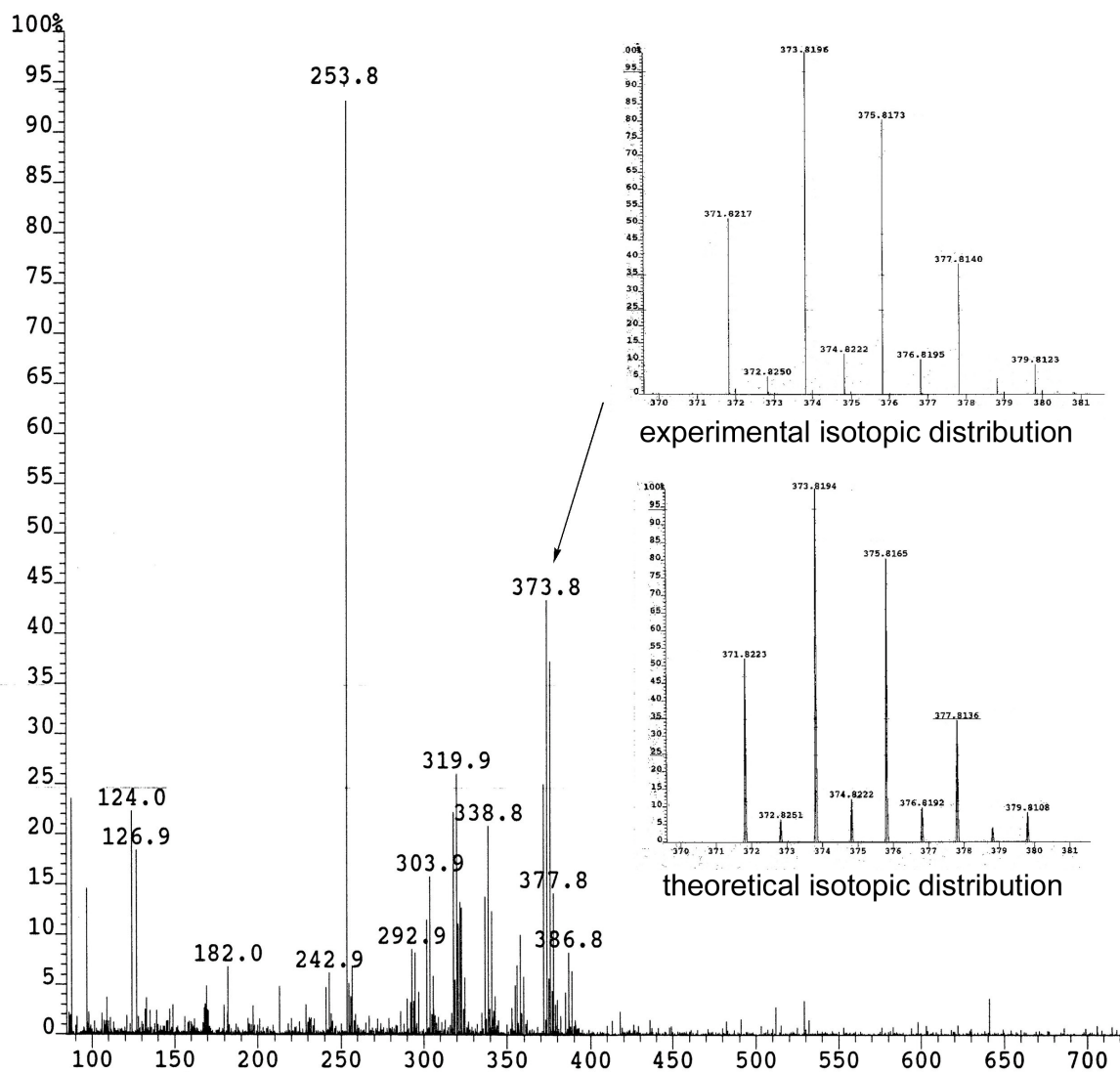


Figure S-4. HRMS (EI) of the perchloro-2,5,8-triazaphenalenyl radical (**1**).

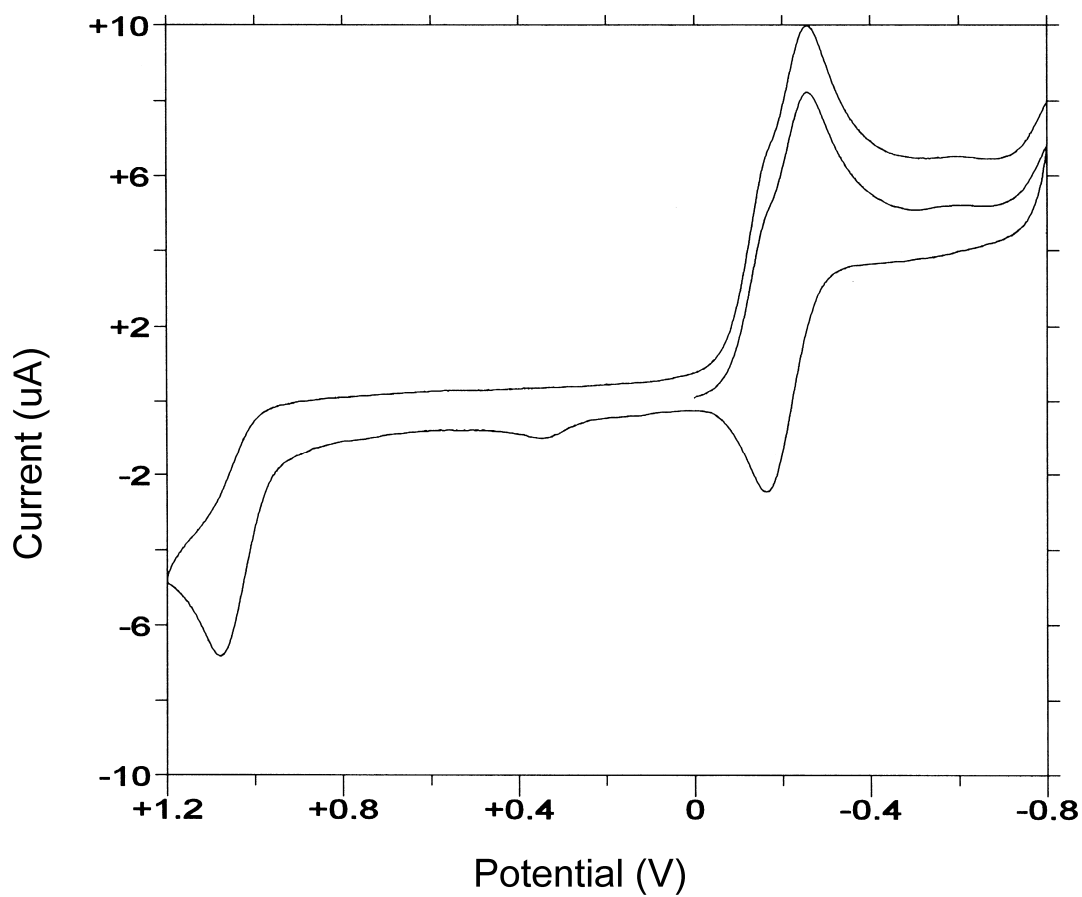


Figure S-5. Cyclic-voltammogram of the perchloro-2,5,8-triazaphenalenyl radical (**1** in 10^{-3} M CH_2Cl_2), with 0.1M $\text{n-Bu}_4\text{NPF}_6$ as supporting electrolyte, Ag pseudo-reference, Fc/Fc^+ internal reference ($E_{\text{Fc/Fc}^+} = 0.42$ V).

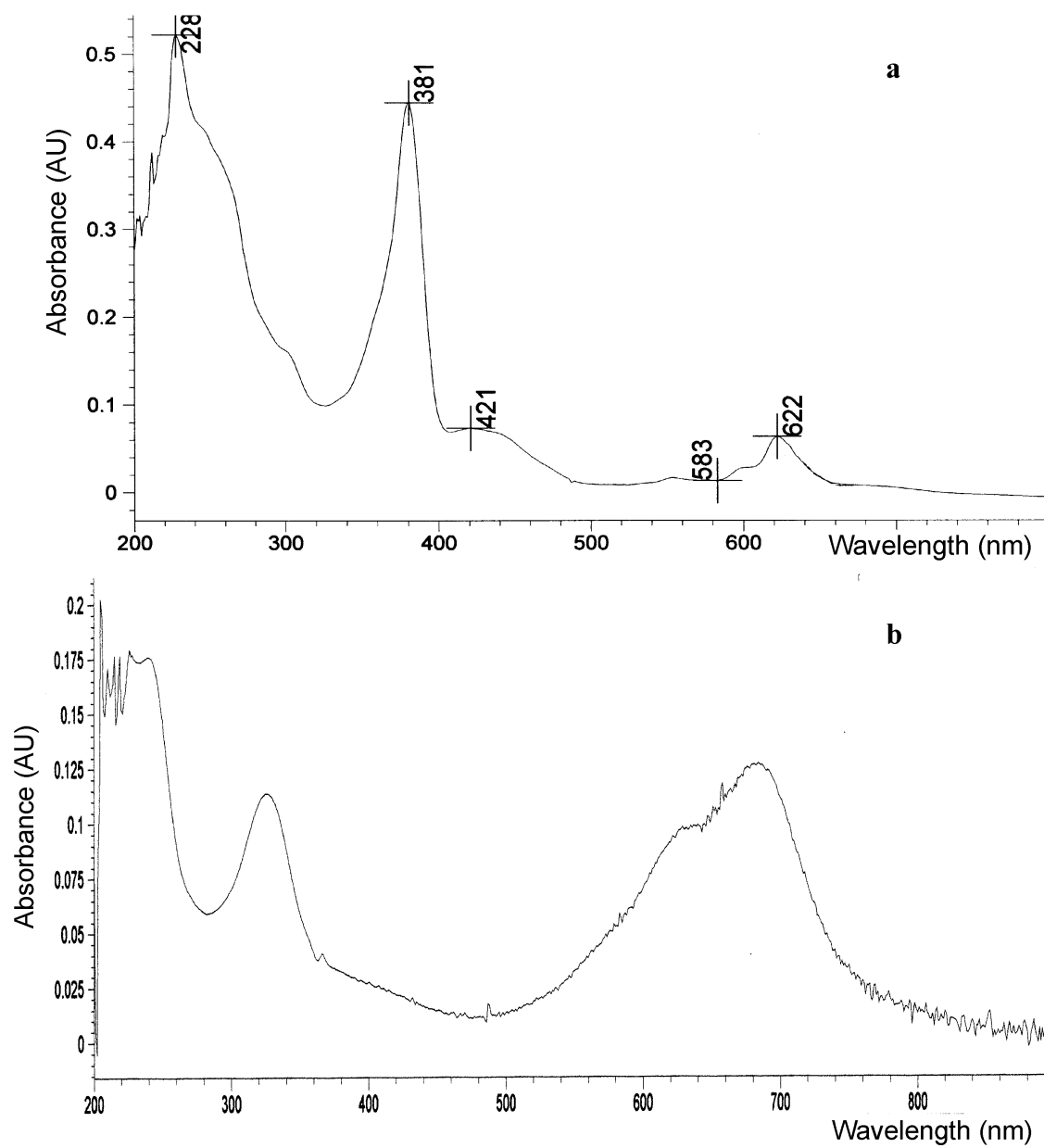


Figure S-6. a). UV-vis spectra of the perchloro-2,5,8-triazaphenalenyl radical **1** (in 4.0×10^{-5} M CH_2Cl_2), **b)** dimer **2** (in 1.0×10^{-5} M CH_2Cl_2).

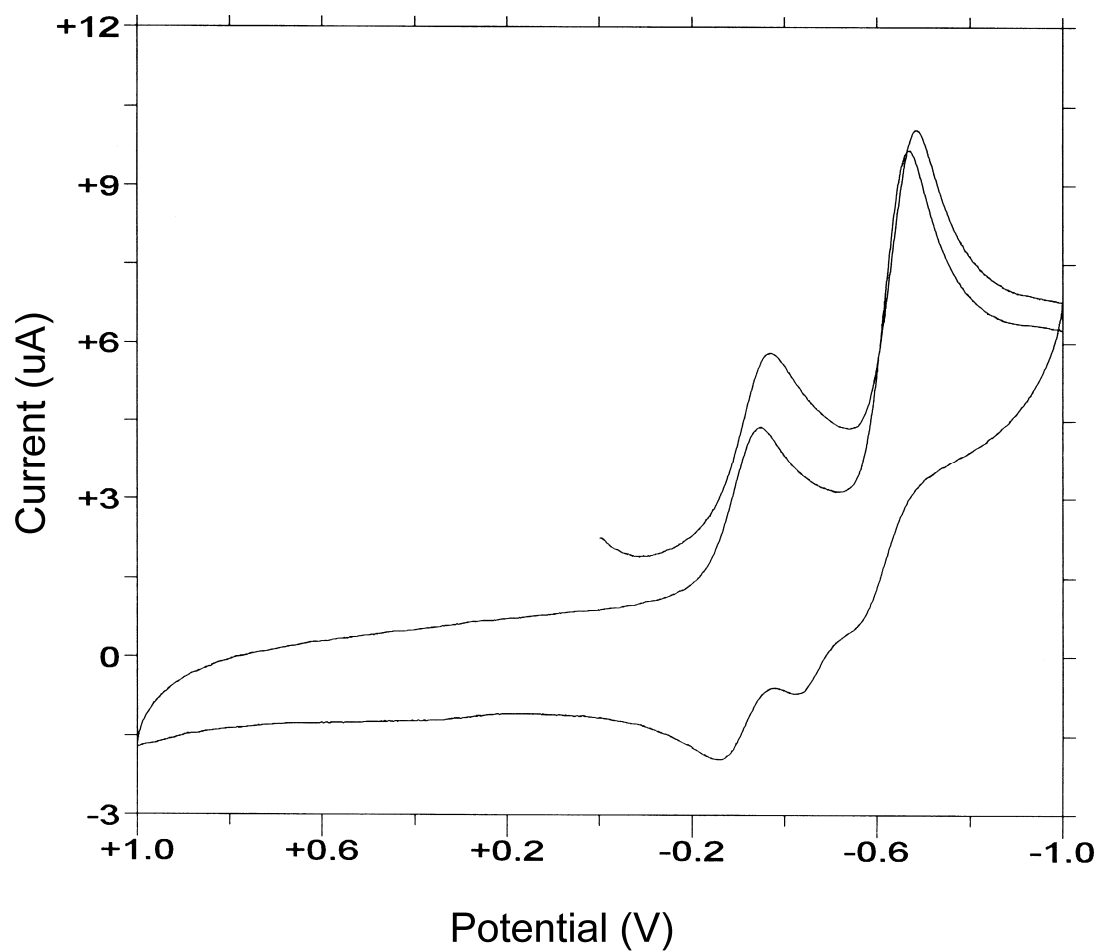


Figure S-7. Cyclic-voltammogram of dimer (**2** in 10^{-3} M CH_2Cl_2), with 0.1M $\text{n-Bu}_4\text{NPF}_6$ as supporting electrolyte, Ag pseudo-reference, Fc/Fc^+ internal-reference ($E_{\text{Fc/Fc}^+} = 0.42$ V).

Table S-1. Temperature dependence of the magnetic susceptibility of the perchloro-2,5,8-triazaphenalenyl radical (**1**).

T (K)	χ (emu/mol)	$1/\chi$ (mol/emu)	χ^*T (emu K/mol)
2.09	7.02E-03	1.42E+02	1.47E-02
7.15	3.35E-03	2.99E+02	2.39E-02
12.20	2.29E-03	4.37E+02	2.79E-02
17.26	1.78E-03	5.60E+02	3.08E-02
22.32	1.49E-03	6.71E+02	3.33E-02
27.37	1.30E-03	7.71E+02	3.55E-02
32.43	1.16E-03	8.61E+02	3.76E-02
37.48	1.06E-03	9.44E+02	3.97E-02
42.54	9.81E-04	1.02E+03	4.17E-02
47.59	9.18E-04	1.09E+03	4.37E-02
52.65	8.67E-04	1.15E+03	4.57E-02
57.70	8.25E-04	1.21E+03	4.76E-02
62.76	7.89E-04	1.27E+03	4.95E-02
67.82	7.59E-04	1.32E+03	5.15E-02
72.87	7.33E-04	1.37E+03	5.34E-02
77.93	7.10E-04	1.41E+03	5.53E-02
82.98	6.89E-04	1.45E+03	5.72E-02
88.038	6.71E-04	1.49E+03	5.91E-02
93.09	6.55E-04	1.53E+03	6.10E-02
98.15	6.41E-04	1.56E+03	6.29E-02
103.20	6.27E-04	1.59E+03	6.48E-02
108.26	6.16E-04	1.62E+03	6.66E-02
113.32	6.05E-04	1.65E+03	6.85E-02
118.37	5.95E-04	1.68E+03	7.04E-02
123.43	5.86E-04	1.71E+03	7.23E-02
128.482	5.77E-04	1.73E+03	7.42E-02
133.54	5.69E-04	1.76E+03	7.60E-02
138.59	5.62E-04	1.78E+03	7.79E-02
143.65	5.55E-04	1.80E+03	7.98E-02
148.70	5.49E-04	1.82E+03	8.16E-02
153.76	5.43E-04	1.84E+03	8.35E-02
158.82	5.38E-04	1.86E+03	8.54E-02
163.87	5.33E-04	1.88E+03	8.73E-02
168.93	5.28E-04	1.90E+03	8.91E-02
173.98	5.23E-04	1.91E+03	9.10E-02
179.04	5.19E-04	1.93E+03	9.29E-02
184.09	5.15E-04	1.94E+03	9.47E-02
189.15	5.11E-04	1.96E+03	9.66E-02
194.20	5.07E-04	1.97E+03	9.85E-02
199.26	5.04E-04	1.99E+03	1.00E-01
204.31	5.00E-04	2.00E+03	1.02E-01

209.37	4.97E-04	2.01E+03	1.04E-01
214.42	4.94E-04	2.02E+03	1.06E-01
219.48	4.91E-04	2.04E+03	1.08E-01
224.54	4.88E-04	2.05E+03	1.10E-01
229.59	4.86E-04	2.06E+03	1.12E-01
234.65	4.83E-04	2.07E+03	1.13E-01
239.70	4.81E-04	2.08E+03	1.15E-01
244.76	4.79E-04	2.09E+03	1.17E-01
249.81	4.76E-04	2.10E+03	1.19E-01
254.87	4.74E-04	2.11E+03	1.21E-01
259.92	4.72E-04	2.12E+03	1.23E-01
264.98	4.70E-04	2.13E+03	1.25E-01
270.04	4.68E-04	2.14E+03	1.26E-01
275.09	4.66E-04	2.14E+03	1.28E-01
280.15	4.65E-04	2.15E+03	1.30E-01
285.20	4.63E-04	2.16E+03	1.32E-01
290.26	4.61E-04	2.17E+03	1.34E-01
295.31	4.60E-04	2.18E+03	1.36E-01
300.37	4.58E-04	2.18E+03	1.38E-01
