Supporting Information for

Triamino-s-triazine Triradical Trications. An Experimental Study of Triazine as a Magnetic Coupling Unit

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General Methods and Materials. All reactions were performed under a dry nitrogen atmosphere. Copper powder (99%, "for organic synthesis"), diphenylether, 4´-aminoacetanilide, *p*-iodoanisole, iodobenzene, diphenylamine, p-anisidine, and cyanuric chloride were purchased from Aldrich Chemical Co. and N,N´-diphenyl-1,4-benzenediamine was purchased from TCI. All chemicals were used without further purification. Thin layer chromatography was performed on Selecto Scientific precoated silica gel F-254 (200 micron) or basic alumina F-254 (200 micron) plates. Column chromatography was performed on silica gel (J.T. Baker, 40 μm flash) or basic alumina (Aldrich, activated Brockmann I, ~150 mesh). Activity III basic alumina was prepared with 6% H_2O.

Infrared spectra were recorded on a Nicolet 360 FT-IR. Nuclear magnetic resonance spectra were recorded on a Bruker AM360. Chemical shifts are reported (δ) relative to TMS for proton spectra and relative to the solvent signal for carbon spectra. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Cyclic voltammetry (CV) was performed on a PAR 273 electrochemical potentiostat (EG&G Instruments). A four-necked CV cell (10 mL) equipped with a Pt disc (1.6 mm diameter) working electrode, a Pt wire counter electrode, and a saturated calomel electrode (SCE) reference was used for routine CV measurements which were carried out under an inert atmosphere. Tetrabutylammonium tetrafluoroborate (Aldrich) was used as supporting electrolyte (0.1M solution) for electrochemical experiments. A capacitor (0.1 μF), connected between the reference electrode and counter electrode, was used to reduce background noise.

ESR Spectroscopy. X-band ESR spectra were recorded on a Varian E-3 spectrometer. All glassware was flame dried prior to use and allowed to cool under a dry nitrogen atmosphere. Solvents used in ESR measurements were purified by standard methods[1] and deaerated with nitrogen or freeze-pump-thaw degassed prior to use. ESR samples of the radical cations were prepared by mixing neutral **4** or **5** with stoichiometric amounts of thianthrenium perchlorate[2] in CH_2Cl_2 to achieve monocation formation or in butyronitrile to achieve trication formation.

Di-p-anisylamine

Di-p-anisylamine is commercially available from Lancaster and TCI or can be prepared in 80% overall yield from Ullmann condensation of 4-methoxyacetanilide and 4-bromoanisole followed by hydrolysis with KOH/EtOH.

2,4,6-Tris(bis(*p*-methoxyphenyl)amino)-1,3,5-triazine (3a)

Di-p-anisylamine (2.60 g, 0.0113 mol) and cyanuric chloride (0.30 g, 0.0016 mol) were heated together at 160 °C with stirring until the fluid mixture solidified (about 1 h). The flask was allowed to cool, and the solid was extracted (2 x 300 mL) with boiling acetone. The acetone insoluble material was recrystallized from toluene to yield colorless needles (0.483 g, 40%): mp 287–288 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 7.04 (d, *J* = 9.0 Hz, 12 H), 6.66 (d, *J* = 9.0 Hz, 12 H), 3.76 (s, 18 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 165.75, 155.66, 136.84, 128.43, 113.41, 55.29; IR (KBr) 3042 (w), 2994 (w), 2955 (w), 2937 (w), 2909 (w), 2836 (w), 1612 (m), 1584 (w), 1543 (s), 1511 (s), 1465 (m), 1426 (s), 1384 (s), 1244 (s), 1180 (m), 1031 (s), 827 (m), 808 (m) cm^{-1}. Anal. Calcd for $C_{45}H_{42}N_6O_6$: C, 70.84; H, 5.56; N, 11.01. Found: C, 70.94; H, 5.72; N, 11.23.

2,4,6-Tris(diphenylamino)-1,3,5-triazine (3b)[3]

Cyanuric chloride (3.00 g, 0.0162 mol) and diphenylamine (22.0 g, 0.130 mol) were heated together at 180–190 °C for 2 hours with stirring. After this time, the hot melt was allowed to cool to 140 °C and then poured into cold water (500 mL). The resulting solid was collected, extracted with boiling acetone (3 x 300 mL) and recrystallized from toluene to give colorless crystalline cubes (9.8 g, 89%): mp 297–298 °C (lit.[4] mp 292.5–293.0 °C). Anal. Calcd for $C_{39}H_{30}N_6$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.48; H, 5.35; N, 14.55.

2,4,6-Tris(di-*p*-bromodiphenylamino)-1,3,5-triazine (3c)

In a 1 L round bottom flask was dissolved **3b** (0.58 g, 1 mmol) in chloroform (450 mL). To this solution, bromine (0.96 g, 0.3 mL, 6 mmol) in chloroform (50 mL) was added dropwise via an addition funnel over 1 h. The resulting mixture was then stirred and heated at reflux for 23 h. The reaction mixture was allowed to cool, and the chloroform was removed in vacuo to give a solid which was recrystallized from toluene to yield colorless needles (1.05 g, 95%): mp 329–330 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.5 Hz, 12 H), 6.91 (d, *J* = 7.5 Hz, 12 H); IR (KBr) 3061 (w), 3037 (w), 1587 (s), 1544 (s), 1500 (s), 1487 (s), 1452 (s), 1388 (s, br), 1010 (m), 822 (m), 804 (m), 752 (m), 693 (m), 510 (w) cm^{-1}. Anal. Calcd for $C_{39}H_{24}N_6Br_6$: C, 44.35; H, 2.29; N, 7.96. Found: C, 44.66; H, 2.17; N, 8.04.

N,N,N´-Triphenyl-1,4-benzenediamine. N,N´-diphenyl-1,4-benzenediamine (5.0 g, 19 mmol), iodobenzene (4.8 g, 24 mmol), anhydrous K_2CO_3 (3.3 g, 24 mmol), copper powder (1.5 g, 24 mmol) and diphenyl ether (5 mL) were heated together at 190 ˚C for 24 hours. (Greater than one mole-equiv of iodobenzene is used to avoid recovery of starting diamine which does not separate easily from desired product.) The mixture was poured into hexane (100 mL), filtered, and absorbed onto a column of basic alumina. Elution with benzene gave N,N,N´,N´-tetraphenyl-1,4-benzenediamine (2.52 g) followed by the triphenyl product (2.23 g, 35 %): mp 128 ˚C (lit.[5] 129 ˚C).

N,N,N´-Tris(4-methoxyphenyl)-1,4-benzenediamine. 4´-aminoacetanilide (5.00 g, 33.3 mmol), *p*-iodoanisole (38.97 g, 166.5 mmol), anhydrous K_2CO_3 (13.8 g, 100 mmol), copper powder (6.35 g, 100 mmol) and diphenyl ether (15 mL) were heated together at 190 ˚C for 48 hours. The mixture was taken up in benzene, filtered, and absorbed onto a column of silica gel. Elution with ethyl ether gave N-[4-[bis(4-methoxyphenyl)amino]-phenyl]-N-(4-methoxyphenyl)-acetamide (13.20 g, 85 %): mp 111 ˚C (lit.[6] 112 ˚C). The amide (8.00 g, 17.1 mmol) was hydrolyzed by KOH (2.31 g, 41.1 mmol) and EtOH (25 mL). The solution was heated at reflux for 24 hours, poured into 400 mL H_2O, and extracted with ethyl ether (3 x 300 mL). The organic layer was dried with K_2CO_3, the volume reduced to ~50 mL, and flashed through a short column of basic alumnia (activity III) with ethyl ether. Removal of the solvent gave N,N,N´-Tris(4-methoxyphenyl)-1,4-benzenediamine[4] (6.80 g, 93 %): mp 87-88 ˚C (no mp previously reported).

2,4,6-Tris[N-[4-(diphenylamino)phenyl]-N-phenylamino]-1,3,5-triazine (4). N,N,N´-Triphenyl-1,4-benzenediamine (1.00 g, 2.97 mmol) and cyanuric chloride (0.0913 g, 0.495 mmol) were heated together at 190 ˚C for approximately one hour. The solidified mixture was ground into a fine powdered, and extracted three times with 100 mL boiling acetone and filtered. Removal of the organic solvent gave pure **4** (0.384 g, 72%): mp 249-50 ˚C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.23-7.15 (m, 24H), 7.05-6.95 (m, 27H), 6.84 (d, J = 8.8 Hz, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 165.83, 147.69, 144.49, 143.65, 138.13, 129.15, 128.26, 128.12, 127.77, 125.06, 124.20, 123.48, 122.62. IR (KBr, cm^{-1}) 3057.8 (w), 3037.3 (w), 1588.9 (s), 1537.9 (s), 1503.8 (s), 1492.4 (s), 1379.3 (s), 1270.3 (s), 751.0 (m), 692.6 (s). Anal. Calcd. for $C_{75}H_{57}N_9$: C, 83.08; H, 5.30; N, 11.63. Found: C, 83.25; H, 5.49; N, 11.61.

2,4,6-Tris[N-[4-bis(4-methoxyphenyl)amino]phenyl-N-(4-methoxyphenyl)-amino]-1,3,5-triazine (5). N,N,N´-tris(4-methoxyphenyl)-1,4-benzenediamine (3.00 g, 7.03 mmol) and cyanuric chloride (0.324 g, 1.76 mmol) were heated together at 190 ˚C for 24 hours. The mixture was taken up in CH_2Cl_2 and washed with aqueous KOH. The organic layer was dried with anhydrous K_2CO_3 and loaded onto a column of basic alumina (activity III). Elution with benzene/ethyl acetate (5:1) gave **5** (1.07 g, 45 %) as a white solid: mp 158-59 °C. ^{1}H NMR (360 MHz, acetone-d_6) δ 7.06 (d, *J* = 8.8 Hz, 6H), 7.00 (d, *J* =8.8 Hz, 6H), 6.95 (d, *J* = 8.9 Hz, 12H), 6.84 (d, *J* = 8.9 Hz, 12H), 6.75 (d, *J* =8.8 Hz, 6H), 6.70 (d, *J* =8.8 Hz, 6H), 3.75 (s, 18H), 3.73 (s, 9H); ^{13}C NMR (90 MHz, acetone-d_6) δ 166.74, 158.04, 156.93, 146.54, 141.99, 138.14, 138.00, 129.89, 128.94, 127.24, 121.19, 115.65, 114.42, 55.80, 55.74. IR (KBr, cm^{-1}) 2828.5 (w), 1540.4 (s), 1503.4 (s), 1428.5 (m), 1381.2 (s), 1240.3 (s), 1175.7 (m), 1034.86 (m). Anal. Calcd. for $C_{84}H_{75}N_9O_9$: C, 74.48; H, 5.58; N, 9.31. Found: C, 74.56; H, 5.58; N, 9.25.

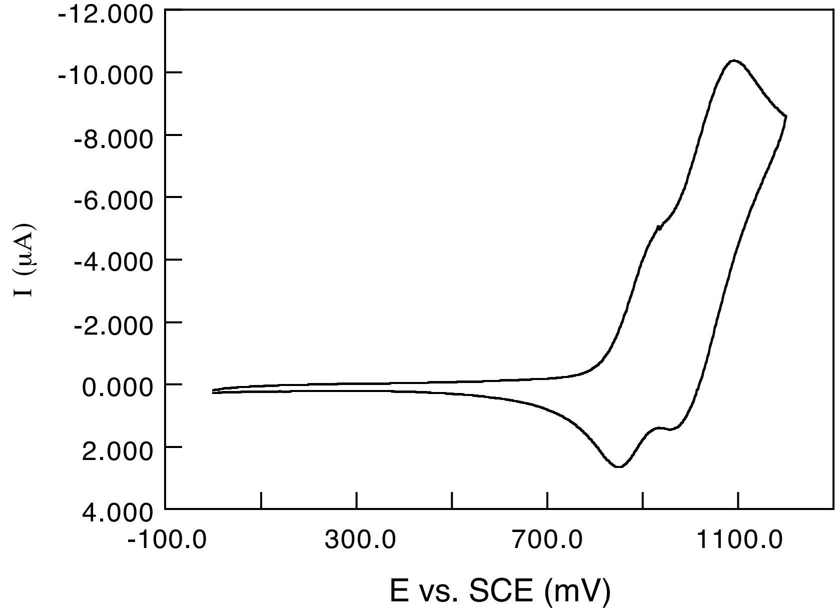

Figure 1S. Cyclic voltammogram of **4** (1.0 mM) in CH_2Cl_2 (0.1 M Bu_4NBF_4) at 20 mVs^{-1} scan rate at 298 K.

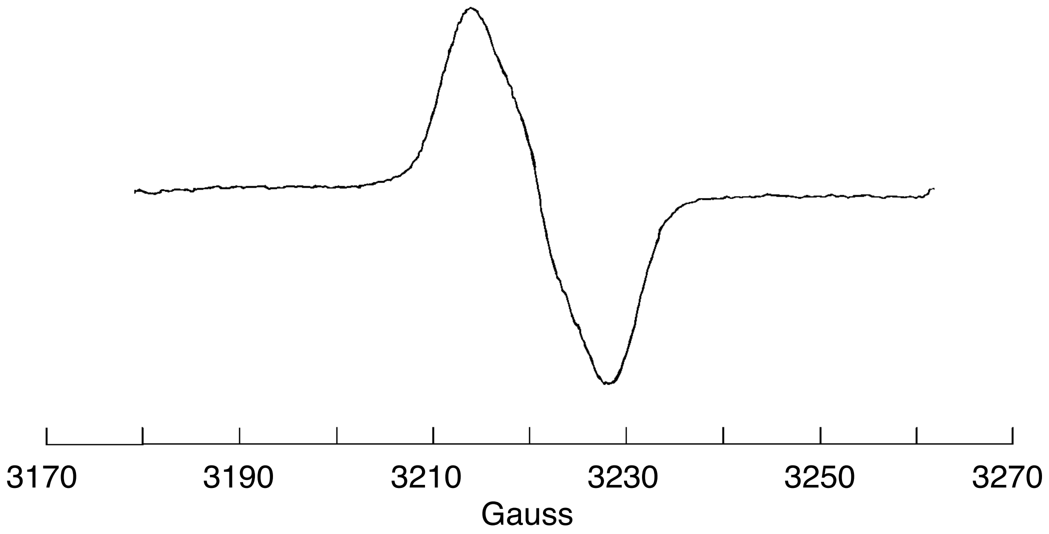

Figure 2S. ESR spectrum of 0.5 mM **$5^+(ClO_4^-)$** in CH_2Cl_2 at 298 K.

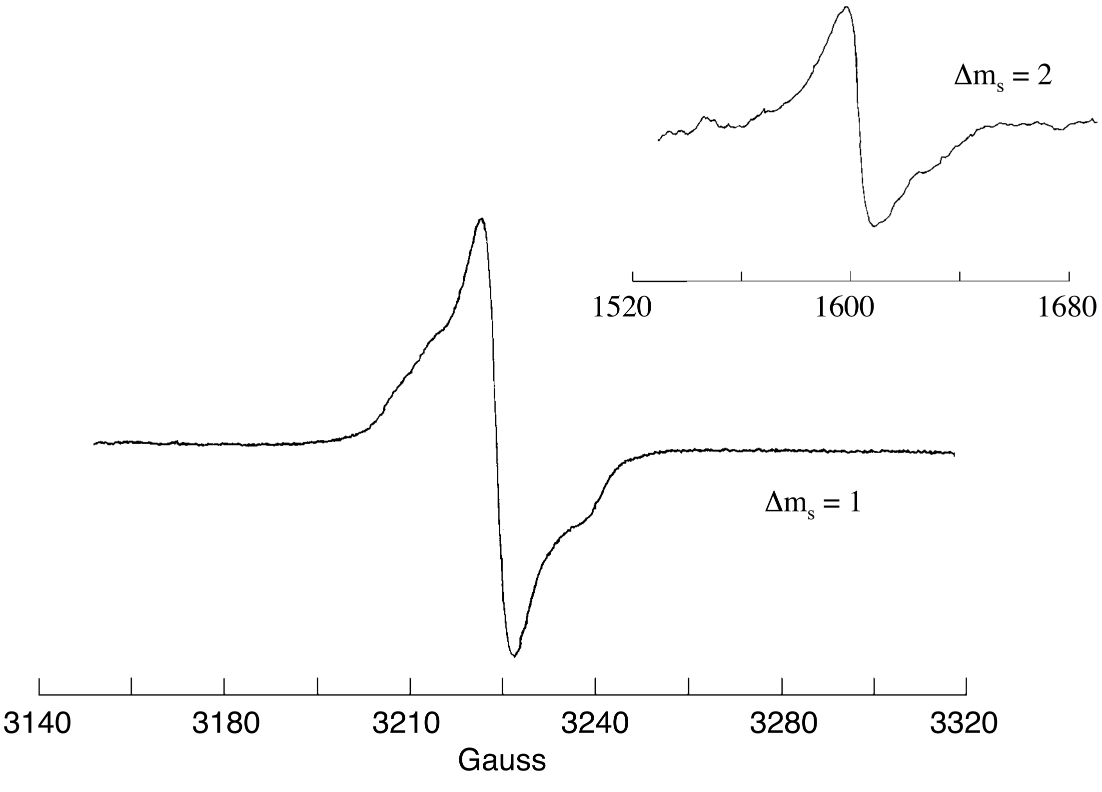

Figure 3S. ESR spectrum of 0.5 mM **$5^{3+}(ClO_4^-)_3$** in PrCN at 90 K.

NMR Magnetic Susceptibility Measurements

Solution magnetic susceptibility measurements were made by the Evans[7] NMR shift method. Spectra were recorded on a 360.136 MHz NMR spectrometer at 301 K in $CDCl_3$ for **5^+** and **5^{3+}** (generated in-situ by oxidation with TH^+ClO_4. The shifts of the TMS signal and μ_{eff} values are given in Table **1S**. For a complete description of the μ_{eff} measurements and calculations see the supporting information of our earlier work.[8]

Table 1S. NMR-derived Susceptibility Data for the cations of **3** at 301 K.

Substrate	Shift (Hz) of the TMS peak[a]				χ_m x 10^{-3}	μ_{eff}
	0.01 M	0.02 M	0.03 M	0.04 M		
$5^+(ClO_4^-)$	18.30	39.69	58.69	72.20	1.22	1.72±0.06
$5^{3+}(ClO_4^-)_3$	33.10 (38.67)	73.14 (72.78)	105.68 (113.99)	145.88 (146.11)	2.42 2.44	2.42±0.05 2.43±0.06

[a] Two values are given where duplicate runs where taken.

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[1] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*;4th ed.; Pergamon Press: New York, 1996.

[2] **Caution!** Thianthrenium perchlorate ($TH^+ClO_4^-$) is a shock sensitive explosive solid and should be handled with due care. For preparation and properties see Murata, Y. Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

[3] The synthesis of melamine substrates was based on the preparation of **3b** as reported in: Zeman, S. *Patent CS* 189514 **1981**.

[4] Pankratov, V. A.; Laktionov, V. M.; Akhmedov, A. I.; Gribkova, P. N.; Pavlova, S.; Bilalov, Y. M.; Vinogradova, S. V.; Korshak, V. V. *Vysokomol. Soedin., Ser. A* **1984**, *26*, 79.

[5] Strohriegl, P.; Jesberger, G.; Heinze, J.; Moll, T. *Makromol. Chem.* **1992**, *193*, 909.

[6] Welzel, P.; Günther, L.; Eckhardt, G. *Chem. Ber.* **1974**, *107*, 3624.

[7] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

[8] Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, *62*, 448.