Supplementary Data

A. Syntheses:

I. 4.7-Diphenyl-1.10-phenathroline-1.2-dithiolato-*ortho*-carborane platinum(II), [Pt(dpphen)(dtoc)].

1.2-dithiolato-*closo*-1.2-dicarbadodecaborane(12) was synthesized according to published procedure (see Smith. H.D.. Obenland. C.O., Papetti. S. *Inorg. Chem.* **1966**, *5*, 1013 & Nakamura. H., Aoyagi, K.. Yamamoto. Y. *Inorg. Chem.* **1997**, *62*, 780). I was synthesized by reacting 1,2-dithiol-*ortho*-carborane with 2 equivalents of Proton Sponge and Pt(dpphen)Cl$_2$ in dry CH$_2$Cl$_2$ for 3.5 hours (Yield 82%). Mass Spect. of **1** exhibits a typical pattern for polyhedral borane compounds with a multiplet at 733.8 m/z corresponding to the molecular weight of the product. ^{1}H NMR (CDCl$_3$) δ 8.43 (d, 2H), 7.53 (s, 2H), 7.24 (d, 2H), 7.06-7.08 (m, 10H), 1.2-3.3 (m. 10H. BH). Anal. Calc. C. 45.07; H. 3.78; N. 3.62. Found C. 44.94; H, 3.93; N, 3.84.

II. 4.7-Diphenyl-1,10-phenathroline-3.5-di-*tert*-butylbenzene-1.2-dithiolate. platinum(II), [Pt(dpphen)(dtbdt)].

4.7-Diphenyl-1,10-phenathrolineplatinum(II) dichloride (0.9036 g; 1.510 mmol) was suspended in 250 mL of dichloromethane. A solution of excess 3.5-di-t-butylbenzenedithiol. and Proton Sponge (0.360 g) was added to the suspension, which immediately turned from yellow to green. The mixture was heated to reflux for 5 hours during which time the solution became dark blue. Removal of the solvent by rotary evaporation yielded a dark blue residue which was dissolved in dichloromethane. Purification by column chromatography on silica gel (1:1 benzene/dichloromethane) yielded a purple solid of analytical purity (yield 25%). ^{1}H NMR (CDCl$_3$) δ 9.5 (d, 1H), 9.4 (d. 1H). 7.9 (s. 2H). 7.6 (m. 2H). 7.5 (m. 8H). 7.4 (m, 2 H), 7.3 (s, 1H), 7.2 (s, 1H), 1.7 (s, 9H). 1.3 (s, 9H). FAB-MS m/z 779.2 (M+). Anal. Calcd for C$_{38}$H$_{36}$N$_2$S$_2$Pt: C. 58.52; H. 4.65; N. 3.59. Found C. 58.65; H, 4.70; N. 3.51.

III. 4,7-Diphenyl-1,10-phenathroline-3,5-di-*tert*-butyl-1.2-catecholate platinum(II), [Pt(dpphen)(dtbc)].

Pt(dpphen)(dtbc) was synthesized by reacting di-*tert*-butyl catechol with KOH (2 eq. in MeOH) and Pt(dpphen)Cl$_2$ in refluxing CH$_2$Cl$_2$ for 24 hours (yield 74%). ^{1}H NMR (CD$_2$Cl$_2$) δ 9.59 (m. 2H). 8.02 (s. 2H). 7.79 (m. 2H). 7.64-7.59 (m. 11H). 7.57 (s. 1H). 1.57 (s. 9H). 1.35 (s. 9H). Anal. Calc. C. 61.03; H. 4.85; N. 3.75. Found 60.78; H, 4.91; N. 3.68.

B. Optical Properties of the Metal Chromophores

Metal Chromophore	λ_{max} nm (M^{-1} cm^{-1}) in 2-Me-THF	Emission max in 2-Me-THF (RT)
I	460 (1.1×10^4)	594
II	634 (8.3×10^3)	810
III	657 (1.1×10^4)	no emission observed

Solvatochromic Property of **I**

solvent	E^N_T	λ_{max} nm	M^{-1} cm^{-1}
C_6H_6	0.111	482	5.14×10^3
2-CH_3-THF	0.179	457	9.05×10^3
$CHCl_3$	0.259	460	9.23×10^4
CH_2Cl_2,	0.309	454	10.4×10^4
$(CH_3)_2CO$	0.355	446	11.6×10^4
CH_3CN	0.460	437	7.31×10^3
CH_3NO_2	0.481	437	9.31×10^3
C_2H_5OH	0.654	420	11.1×10^3

Solvatochromic Property of **II**

solvent	E^N_T	λ_{max} nm	M^{-1} cm^{-1}
C_6H_6	0.111	684	8.32×10^3
2-CH_3-THF	0.179	660	10.8×10^3
$CHCl_3$	0.259	634	8.34×10^4
CH_2Cl_2,	0.309	612	8.14×10^4
$(CH_3)_2CO$	0.355	613	9.24×10^4
DMSO	0.444	590	9.63×10^4
CH_3CN	0.460	581	8.55×10^3
CH_3NO_2	0.481	583	9.12×10^3

Solvatochromic Property of **III**

solvent	E^N_T	λ_{max} nm	M^{-1} cm^{-1}
C_7H_8	0.099	719	9.45×10^3
2-CH_3-THF	0.179	680	7.62×10^3
$CHCl_3$	0.259	657	1.52×10^4
CH_2Cl_2,	0.309	621	6.71×10^4
$(CH_3)_2CO$	0.355	625	1.15×10^4
CH_3CN	0.460	589	4.71×10^3
CH_3NO_2	0.481	583	8.06×10^3
CH_3OH	0.762	558	6.37×10^3

C. EFISH Measurements

The conventional EFISH (Electric field Induced Second Harmonic) technique was used to measure the quadratic hyperpolariability of the compounds [J.L. Oudar, J. Chem. Phys. 67 (1977) 446; and reference 31]. The initial wavelength 1.064 mm of a Nd:Yag laser was shifted to 1.907 mm by stimulated Raman scattering in a high pressure hydrogen cell. DC electric field pulses with amplitude up to 30 kV/cm were applied to the solutions placed in a wedge cell. The second harmonic signals were calibrated to a quartz wedge (quadratic hyperpolarizability taken equal to 1.1 10^{-19} esu at 1.907 mm). Experimental details and analytical expressions for the mean microscopic hyperpolarizability γ are given in Oudar 1977. Neglecting the purely electronic contribution (appropriate for medium sized conjugated molecules) leads to the expression

$$\gamma = \frac{\mu\beta(2\omega)}{5kT}$$

where kT is the Boltzmann factor, μ_g the dipole moment of the molecular ground state, β stands for the vector part of tensor $\beta_{ijk}(2\omega)$. In the two level approximation the dispersion dependence of the quadratic hyperpolarizability $\beta(\omega)$ is described by the simple dispersion factor

$$\beta(\omega) = \frac{\omega_{max}^4}{(\omega_{max}^2 - \omega^2)(\omega_{max}^2 - 4\omega^2)} \beta(0)$$

where the ω's are the pulsations corresponding respectively to the fundamental laser wavelength λ and λ_{max} and $\beta(0)$ the intrinsic static hyperpolarizability .