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Supramolecular Photochemistry and Photophysics. Adducts of $Pt(bpy)(NH_3)_2^{2+}$ with Aromatic Crown Ethers

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Abstract: We report results of an investigation concerning absorption spectra, emission spectra, luminescence lifetimes, electrochemical properties, and photochemical behavior of $Pt(bpy)(NH_3)_2^{2+}$ (bpy = 2,2′-bipyridine) and its adducts with the following crown ethers in CH_2Cl_2 and CH_3CN solution: 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8), dibenzo-30-crown-10 (DB30C10), dibenzo-36-crown-12 (DB36C12), bis(*m*-phenylene)-32-crown-10 (BMP32C10), bis(*p*-phenylene)-34-crown-10 (BPP34C10), and dinaphtho-30-crown-10 (DN30C10). Adduct formation with the aliphatic crown ether 18C6 does not change the photochemical and photophysical properties of the $Pt(bpy)(NH_3)_2^{2+}$ complex. By contrast, adduct formation with the aromatic crown ethers causes (i) a strong decrease of the crown ether absorption band and of the ligand (bpy)-centered absorption bands of $Pt(bpy)(NH_3)_2^{2+}$ in the 260–330-nm region, (ii) the appearance of a new broad absorption band in the 340–450-nm region, (iii) the complete or partial quenching of the crown ether fluorescence and of the ligand-centered phosphorescence of $Pt(bpy)(NH_3)_2^{2+}$, (iv) the appearance of a new, broad, and short-lived luminescence band in the 550–630-nm region, (v) the quenching of the photoreaction of $Pt(bpy)(NH_3)_2^{2+}$ in CH_2Cl_2, and (vi) a perturbation in the electrochemical reduction potentials. These results are attributed to an electronic interaction, in the ground and excited state, between the bpy ligand of the Pt complex and the aromatic rings of the crowns. The intensity of such electronic interaction depends on the size of the crown ring and on the nature and substitution positions of the aromatic rings present in the crown. The results obtained show that the assembly of a coordination compound into an appropriate supramolecular structure can protect the compound from photoreaction and can profoundly change its spectroscopic, photophysical, and electrochemical properties.

In the field of photochemistry, which is at the crossroads of chemistry, physics, and biology and at the interface between matter and light, the quantitative growth of the past 20 years has been accompanied by profound qualitative changes. The interest of the research workers has progressively moved from photoreactions taking place inside molecules (*intra*molecular photochemistry)[2,3] to processes taking place between long-lived excited states and suitable reaction partners (*inter*molecular electron- and energy-transfer processes).[4-11] In the past few years a trend to study artificial assemblies of two or more molecular components (*supra*molecular photochemistry)[12,13] has also emerged with the dual aim of making progress toward the understanding of photobiological processes and the design of artificial systems capable of performing useful functions.

In the area of supramolecular photochemistry one can distinguish (Figure 1) systems made by (i) covalently linked molecular building blocks (e.g., diads, triads, tetrads, polynuclear complexes)[14-18] and (ii) molecular entities associated by electrostatic interaction, hydrogen bonds, or other intermolecular forces (host–guest systems, ion-pair species, second-sphere coordination complexes).[12,18-21]

Continuing our investigations on systems of the latter type,[22] we have now examined in a systematic way the photochemical and photophysical behavior of the host–guest species originating from $Pt(bpy)(NH_3)_2^{2+}$ and crown ethers of different size and structure (Figure 2).[23]

Experimental Section

Chemicals. $[Pt(bpy)(NH_3)_2](PF_6)_2$ (bpy = 2,2′-bipyridine) has been prepared from $Pt(bpy)Cl_2$ following a slightly modified literature procedure.[24a,b] The purity of the compound was checked by elemental analysis and by comparison with the known absorption spectrum.[24c] The crown ethers 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and dibenzo-24-crown-8 (DB24C8) were obtained from Aldrich. The other

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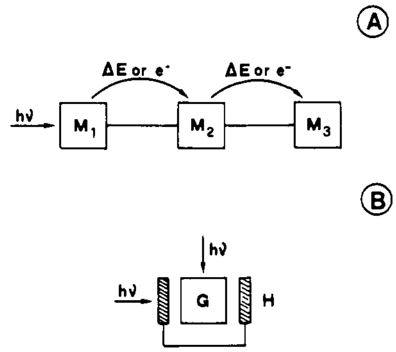

Figure 1. Schematic representation of two types of supramolecular systems: covalently linked molecular building blocks (A); host-guest systems (B).

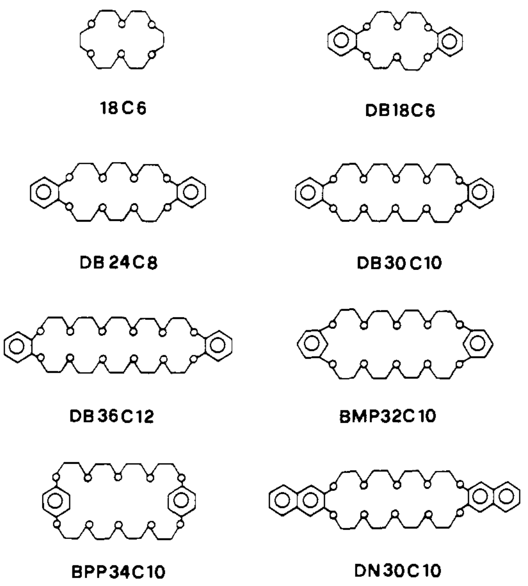

Figure 2. Structures of the crown ethers and abbreviations used.

Table I. Absorption, Emission, and Lifetime Data of the Aromatic Crown Ethers in CH_2Cl_2

	absorption[a] 298 K		emission			
			298 K[b]		77 K[c]	
aromatic crown ethers	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	τ,[d] ns	λ_{max}, nm	τ, s
DB18C6	277	5650	310	0.4		
DB24C8	277	5200	308	0.5	460	$>10^{-3}$[e]
DB30C10	277	4400	308	0.4		
DB36C12	277	4700	308	0.7	460	$>10^{-3}$[e]
BMP32C10	275	3700	300	1.0	410	$>10^{-3}$[e]
	281	3300				
BPP34C12	290	5300	320	0.6	420	$>10^{-3}$[e]
DN30C10	268	8900	339	9.6	485	1.6[d]
	274	8100				
	310	4400				
	315	3800				

[a] Only the absorption band above 250 nm are reported. [b] Fluorescence. [c] Phosphorescence. [d] Estimated uncertainty ±10%. [e] See text.

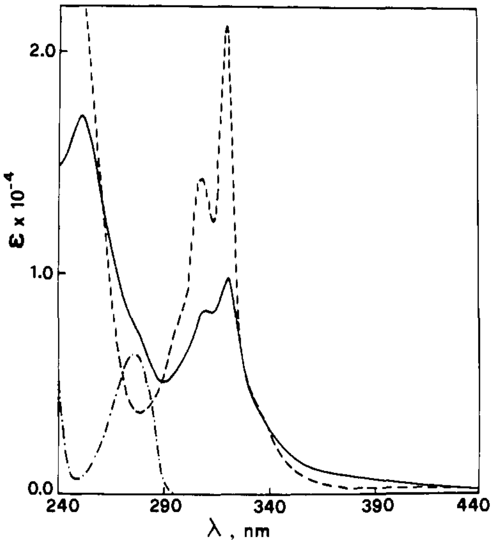

Figure 3. Absorption spectra in CH_2Cl_2: DB30C10 (-·-); Pt(bpy)$(NH_3)_2^{2+}$·18C6 (---); Pt(bpy)$(NH_3)_2^{2+}$·DB30C10 (—).

crowns, i.e., dibenzo-30-crown-10 (DB30C10), dibenzo-36-crown-12 (DB36C12), dinaphtho-30-crown-10 (DN30C10), bis(*m*-phenylene)-32-crown-10 (BMP32C10), and bis(*p*-phenylene)-34-crown-10 (BPP34C10) were prepared following literature procedures.[25] Tetrabutylammonium tetrafluoroborate and tetrabutylammonium perchlorate were Fluka products. Acetonitrile (AN) was an RPE Carlo Erba product. Dichloromethane (CH_2Cl_2) was a Merck product. Both were distilled before use on P_2O_5. Butyronitrile (Fluka) was distilled together with CH_2Cl_2 to remove water traces. The solid 1:1 adducts between [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$ and DB24C8 or DB30C10 were prepared as previously reported.[18] The other adducts were obtained in solution by adding [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$ to a stoichiometric amount or an excess of crown ether dissolved in the selected solvent. The concentration of the platinum complex was 1.0×10^{-4} M unless otherwise noted.

Equipment. Absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer. Uncorrected emission spectra were recorded with a Perkin Elmer 650-40 spectrofluorimeter. Corrected excitation spectra were obtained with a Perkin Elmer LS 5 spectrofluorimeter that was also used to obtain luminescence lifetimes in the 5 μs-10 ms time region. A Nd:YAG DLPY4 JK laser and an Edinburgh single-photon-counting apparatus were used for longer and shorter lifetimes, respectively. In all cases the experimental error on the lifetime values is estimated to be ±10%. In the Edinburgh system the flash lamp was filled with H_2, and a monochromator was used to select the excitation wavelength. The instrument response function was deconvoluted from the emission data to obtain an undisturbed decay that was then fitted by a least-squares method on an IBM PC. Each sample gave rise to single-exponential decays. For very low intensity emissions taking place with $\tau \leq 10$ ns lifetimes, values could not be obtained because it was impossible to separate the luminescence from the scattering of the exciting light. Luminescence quantum yields were measured by using $Ru(bpy)_3^{2+}$ in aerated aqueous solution ($\Phi_{em} = 0.028$[26]) as a standard for room-temperature experiments and were corrected for different refractive index of the solvents. At 77 K, the standard was $Rh(bpy)_3^{3+}$ ($\Phi_{em} = 1.0$[27]) in butyronitrile. In both cases the estimated error is ±20%. Photochemical experiments were carried out with a medium-pressure Q 400 Hanau mercury lamp whose light was filtered with a Oriel interference filter ($\lambda_{max} = 313$ nm, $T_{max} = 16\%$). The solutions were irradiated in a spectrophotometric cell (capacity, 3 mL; optical path, 1 cm) housed in a thermostated cell holder and stirred with a magnetic stirrer. The incident light intensity (1.6×10^{-7} $N h\nu$/min) was measured by the ferric oxalate actinometer.[28] Cyclic voltammetry was performed with an Amel 448/XA oscillographic polarograph on Ar-purged acetonitrile and dichloromethane solutions containing 0.1 M tetrabutylammonium tetrafluoborate and tetrabutylammonium perchlorate, respectively, as supporting electrolyte. The working electrode was a platinum microelectrode, the counter electrode was a platinum wire, and a standard calomel electrode (SCE) was the reference electrode. All the experiments were performed at room temperature (~25 °C), unless otherwise noted.

Results

The experiments were carried out in CH_2Cl_2, acetonitrile, or butyronitrile, [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$ is soluble in acetonitrile and

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Table II. Absorption, Emission, and Lifetime Data of $[Pt(bpy)(NH_3)_2](PF_6)_2$ and Its Adducts with Crown Ethers[a]

	absorption[b] 298 K		emission 298 K			emission 77 K	
	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	τ,[c] ns	$10^{-4}\Phi$[d]	λ_{max}, nm	τ,[c] μs
$[Pt(bpy)(NH_3)_2](PF_6)_2$	319[e]	18 000	488[e,f]	<10[g]	2	453[f,h]	25[h]
	307[e]	12 500					
$Pt(bpy)(NH_3)_2^{2+}\cdot$18C6	319	21 000	488[f]	100	25	486[f]	25
	308	13 300					
$Pt(bpy)(NH_3)_2^{2+}\cdot$DB18C6	319	15 000	488[f]	<10[g]	≤1	492[f]	25
	308	10 000	575	<10[f]	1		
$Pt(bpy)(NH_3)_2^{2+}\cdot$DB24C8	319	13 200	585	<10[f]	5	487[f]	26
$Pt(bpy)(NH_3)_2^{2+}\cdot$DB30C10	320	9 900	585	<10[f]	5	493[f]	10
	309	8 400					
$Pt(bpy)(NH_3)_2^{2+}\cdot$DB36C12	320	14 400	585	<10[g]	3	488[f]	23
$Pt(bpy)(NH_3)_2^{2+}\cdot$BMP32C10	319	9 700	560	<10[g]	3	496[f]	31
	312[i]	9 000					
$Pt(bpy)(NH_3)_2^{2+}\cdot$BPP34C10	321	10 900	600	<10[g]	2	490[f]	10
$Pt(bpy)(NH_3)_2^{+}\cdot$DN30C10	320	9 000	555	30	75	498[f]	30
	309	7 600					

[a] In CH_2Cl_2, unless otherwise noted. [b] Bpy-centered absorption in the 300–320-nm region. For other absorption bands, see text. [c] Estimated uncertainty ±10%. [d] Approximate values obtained by comparison of the intensity of the emission maxima and $\Phi = 5.0 \times 10^{-4}$ (±20%) for the adduct with DB30C10. [e] AN solution. [f] Structured band. [g] See text. [h] Butyronitrile solution. [i] Shoulder.

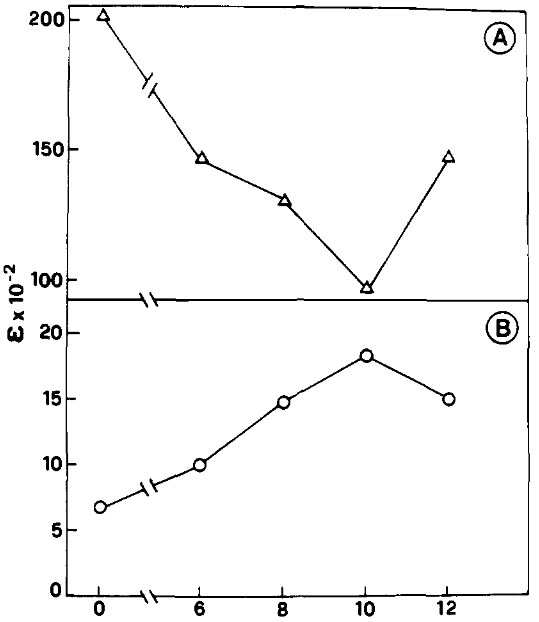

Figure 4. Plots of the extinction coefficients at 319 nm (A) and 350 nm (B) for the adducts of the dibenzo–crown ethers as a function of the number of the ring oxygens.

butyronitrile but not in CH_2Cl_2. However it can be dissolved in CH_2Cl_2 by crown ethers, including the aliphatic 18C6.

For the adducts that were prepared in the solid state, the same results were obtained by dissolving the adduct or mixing equimolar amounts of solutions of the two components. The other adducts were obtained in solution, mixing stoichiometric amounts[24b] of $[Pt(bpy)(NH_3)_2](PF_6)_2$ and crown ether. For CH_2Cl_2 solutions, an excess (2–5 times) of crown ether was used in the case of 18C6 and DB18C6.

Absorption Spectra. The absorption spectrum of 18C6 in CH_2Cl_2 does not shown any band above 240 nm. The aromatic crown ethers show bands in the 260–330-nm region (Table I). The spectrum of DB30C10 is shown in Figure 3. In the same figure one can also see the absorption spectrum of the $Pt(bpy)(NH_3)_2^{2+}\cdot$18C6 adduct in CH_2Cl_2, which is essentially coincident with the absorption spectrum of $[Pt(bpy)(NH_3)_2](PF_6)_2$ in AN solution. The spectra of the adducts of $Pt(bpy)(NH_3)_2^{2+}$ with the aromatic crown ethers (Table II) were substantially different from the summation of the spectra of the two components, as is also shown in the example of Figure 3. The most important changes are (i) a strong decrease in the intensity of the aromatic crown ether band and of the ligand-centered bpy band of the complex and (ii) the appearance of a new band or of an absorption tail in the region above 340 nm. The degree of these changes varied for the various adducts, as shown by Figure 4, which reports the values of the extinction coefficients of the maximum of the bpy-centered band at 319 nm and of the tail at 350 nm for the adducts of the homogeneous family of bis(σ-benzo)–crown ethers. For adducts with BPP34C10 and DN30C10 a new band is clearly present in the 340–450-nm region, as shown in Figure 5. In AN solution the spectral changes caused by adduct formation were qualitatively the same but much smaller in intensity. In going from CH_2Cl_2 to AN as a solvent the low-energy absorption moves to the blue. In the case of BPP34C10 adduct this causes the disappearance of the absorption maximum.

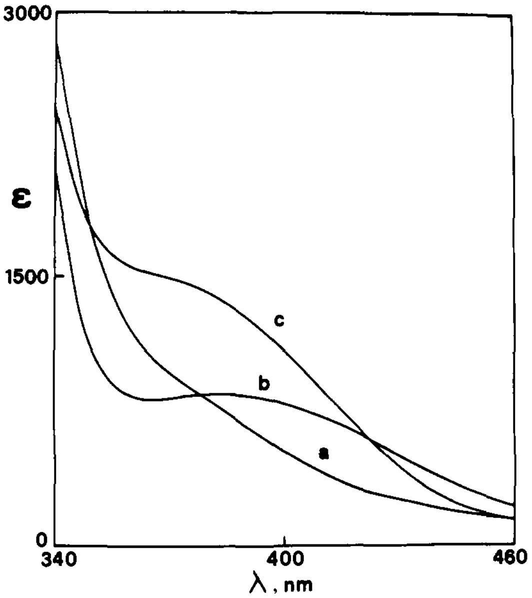

Figure 5. Absorption spectra in CH_2Cl_2 above 340 nm for the adducts with DB30C10 (a), BPP34C10 (b), and DN30C10 (c).

Luminescence. In CH_2Cl_2 solution at room temperature all the aromatic crowns exhibited a fluorescence emission in the UV region characteristic of their dimethoxybenzene or -naphthalene moieties[29] (Table I). The fluorescence band of DB30C10 is shown in Figure 6. For most of the aromatic crowns a phosphorescence emission in the spectral range 420–500 nm was observed at 77 K (Table I). In the case of DN30C10 the phosphorescence was moderately strong, with τ = 1.6 s. For the other crowns, weakness

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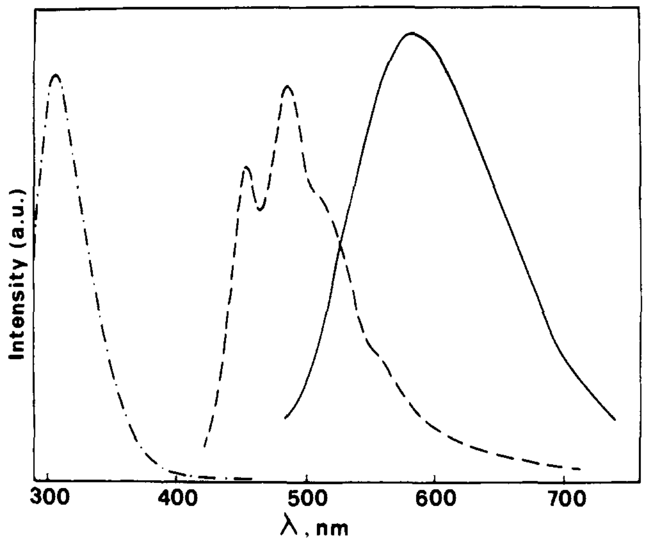

Figure 6. Emission spectra in CH_2Cl_2 at 298 K: DB30C10 (–··–); $Pt(bpy)(NH_3)_2^{2+}$·18C6 (– – –); $Pt(bpy)(NH_3)_2^{2+}$·DB30C10 (—).

of the emission and the high light scattering of the opaque matrix prevented an exact measurement of the phosphorescence lifetime, which, in any case, is longer than 10^{-3} s.

The $Pt(bpy)(NH_3)_2^{2+}$ complex in AN solution at room temperature shows a structured luminescence band with maximum at 488 nm and lifetime ≤ 10 ns. In rigid butyronitrile matrix at 77 K the structure of the emission band is more pronounced, and the highest intensity feature is that at highest energy (453 nm). Under such conditions the luminescence lifetime is 25 μs and the luminescence quantum yield is 0.50.

$[Pt(bpy)(NH_3)_2](PF_6)_2$ is not soluble in CH_2Cl_2, but as mentioned above, it can be solubilized in the presence of an excess of the aliphatic 18C6 crown ether. At 77 K in CH_2Cl_2 (opaque) matrix, the emission spectrum of the $Pt(bpy)(NH_3)_2^{2+}$·18C6 adduct is practically identical with that of the free Pt complex in butyronitrile matrix and the luminescence lifetime is the same. The luminescence spectrum in CH_2Cl_2 solution at room temperature (Figure 6) is practically identical with that shown by the free Pt complex dissolved in AN but about 10 times more intense and much longer lived (100 ns).

In CH_2Cl_2 solution at room temperature the adducts between $Pt(bpy)(NH_3)_2^{2+}$ and the various aromatic crowns, with the exception of $Pt(bpy)(NH_3)_2^{2+}$·DB18C6, did not show the luminescence bands of the two components but only a new, broad, low-intensity emission band in the 550–620-nm region. The emission spectrum of the $Pt(bpy)(NH_3)_2^{2+}$·DB30C10 adduct is shown in Figure 6. The maximum of the emission band changes with the solvent, e.g., from 585 to 610 nm for the adduct with DB30C10 and from 600 to 630 nm for the adduct with BPP34C10 in going from CH_2Cl_2 to AN. The emission maxima for the various adducts are shown in Table II. The quantum yield of the luminescence of the $Pt(bpy)(NH_3)_2^{2+}$·DB30C10 adduct was 5.0 × 10^{-4} regardless of the excitation band (λ = 277, 320, and 350 nm). Approximate values of the emission quantum yields for the other adducts were estimate from the relative values of the intensities of their emission maxima (Table II). The emission lifetime could be measured only for the adducts with DN30C10 and 18C6 (Table II). In CH_2Cl_2 at 77 K (opaque matrix) the adducts exhibited only an intense structured band similar to that shown by the free $Pt(bpy)(NH_3)_2^{2+}$ complex.

The $Pt(bpy)(NH_3)_2^{2+}$·DB18C6 adduct in CH_2Cl_2 solution at room temperature showed *both* the structured band characteristic of $Pt(bpy)(NH_3)_2^{2+}$ with maximum at 488 nm *and* a broad band with maximum at 575 nm similar to that exhibited by the other adducts. The relative intensities of the two bands depended on temperature, as shown by Figure 7 where the spectra at 180 and 298 K are reported.

In AN solution at room temperature the equimolecular mixtures of $Pt(bpy)(NH_3)_2^{2+}$ and aromatic crowns showed the crown fluorescence in the 300-nm region, the structured $Pt(bpy)(NH_3)_2^{2+}$ band with maximum at 488 nm, and a broad band in the 550–630-nm region. Addition of an excess of crown ether caused a decrease in the intensity of the 488-nm band and an increase in intensity of the broad emission at longer wavelength. In 1:1 AN–CH_2Cl_2 mixtures, the three bands were still present, but the broad low-energy band became more intense than the structured $Pt(bpy)(NH_3)_2^{2+}$ band.

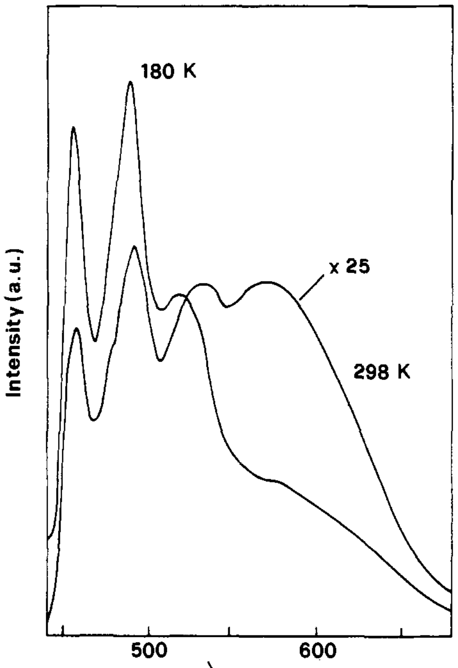

Figure 7. Emission spectra in CH_2Cl_2 of $Pt(bpy)(NH_3)_2^{2+}$·DB18C6 at 180 and 298 K.

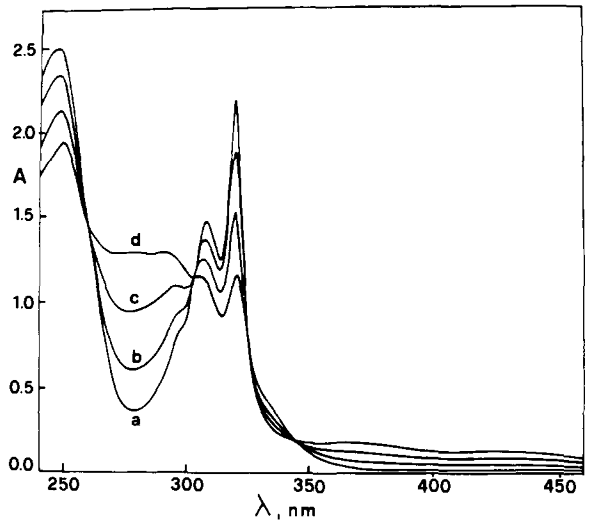

Figure 8. Spectral changes on irradiation of $Pt(bpy)(NH_3)_2^{2+}$·18C6 in CH_2Cl_2 with 313-nm light: t = 0 (a), 30 min (b), 90 min (c), and 190 min (d).

Photochemistry. $Pt(bpy)(NH_3)_2^{2+}$ is almost photoinert in AN but light sensitive in CH_2Cl_2 solution when solubilized by 18C6. The spectral changes observed for $Pt(bpy)(NH_3)_2^{2+}$·18C6 in CH_2Cl_2 solutions irradiated at 313 nm are shown in Figure 8. The actual nature of the photoreaction was not investigated in detail, but extraction with *n*-heptane showed that bpy is not released. Limiting values for the quantum yield of reactant disappearance could be obtained from the change in absorption at 319 nm for short irradiation time. On the assumption that the product does not absorb at that wavelength, the quantum yield is 8 × 10^{-3}. From the almost plateau value reached by the absorbance at 318

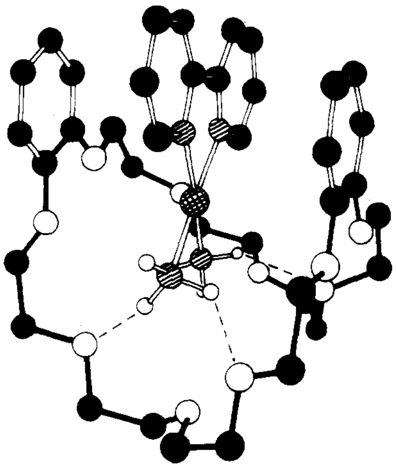

Figure 9. Skeletal representation of the X-ray structure of Pt(bpy)(NH_3)$_2^{2+}$·DB30C10 (from ref 24d).

nm after long irradiation periods, a likely more correct value of 1.4 × 10^{-2} was obtained.

For the adducts of Pt(bpy)(NH_3)$_2^{2+}$ with DB24C8, DB30C10, DB36C12, BMP32C10, BPP34C10, and DN30C10 in CH_2Cl_2 solution no spectral changes were observed even after prolonged irradiation, whereas the adduct with DB18C6 exhibited photoinduced spectral changes similar to those shown by the adduct with 18C6.

Electrochemistry. In AN solution, Pt(bpy)(NH_3)$_2^{2+}$ shows no oxidation wave below +2.0 V and two reduction waves with E_p^c −1.13 and −1.80 V. For the first reduction process no anodic peak was observed, whereas for the second one an anodic peak was present, displaced by 120 mV from the cathodic peak. A quite similar electrochemical behavior is observed when Pt(bpy)(NH_3)$_2^{2+}$ is solubilized in CH_2Cl_2 by the aliphatic 18C6.

In the aromatic crown ethers there are dimethoxybenzene or -naphthalene units which are expected[30] to undergo oxidation below +2.0 V. We have examined the electrochemical behavior of DB30C10 in AN solution, and we have found an irreversible oxidation wave at +1.45 V and no reduction wave, as was already known to happen for 1,2-dimethoxybenzene.[30] No redox wave was observed in the potential range +2/−2 V for CH_2Cl_2 solution.

In CH_2Cl_2 solution the adduct Pt(bpy)(NH_3)$_2^{2+}$·DB30C10 showed no oxidation peak and two reduction waves at −1.40 and −1.80 V. In AN solution a more complex behavior was observed, with two overlapping irreversible oxidation waves around +1.6 V, two partially overlapping reduction waves with peaks at −1.13 and −1.40 V, a wave at −1.80 V, and a fourth wave at −2.0 V. Addition of an excess of DB30C10 caused a decrease in the intensity of the peak at −1.13 V and an increase of that at −1.40 V.

Discussion

The formation of 1:1 adducts between Pt(bpy)(NH_3)$_2^{2+}$ and 18C6, DB3*n*C*n* (*n* = 6, 8, 10, 12), and DN30C10 in CH_2Cl_2 solution and in the solid state was previously demonstrated (see, e.g., Figure 9).[23] The high stability of the adducts with the aromatic crowns in CH_2Cl_2 at room temperature is shown by the absence of the luminescence bands of the two components.

In AN or AN/CH_2Cl_2 mixtures, the adducts are in equilibrium with substantial amounts of free components, as indicated by the behavior of the absorption and emission spectra and by the electrochemical results. For the Pt(bpy)(NH_3)$_2^{2+}$·DB30C10 adduct an association constant of ~200000 M^{-1} can be evaluated in AN solution from both absorption[24b] and emission spectra titrations. This means that under our experimental conditions (total concentration of the dissolved adduct = 1.0 × 10^{-4} M) approximately 20% of the adduct is dissociated into its components.

Since [Pt(bpy)(NH_3)$_2$](PF_6)$_2$ can be solubilized in CH_2Cl_2 by the aliphatic crown ether 18C6, the main driving force for the association of the adduct is likely the formation of hydrogen bonds between the oxygens of the crown ethers and the hydrogens of the NH_3 ligands of the complex. This is confirmed by the X-ray structure[23] of the adducts with DB24C8, DB30C10, and DN30C10, where the distance between the nitrogens of the amine ligands and the oxygens of the crown are those required for H-bond formation. With the aromatic crowns, however, there is also an interaction between the aromatic rings of the crowns and the bpy ligand of the complex, which leads the crown to assume the U shape observed in the X-rays structure of the Pt(bpy)(NH_3)$_2^{2+}$·DB30C10 (Figure 9) and Pt(bpy)(NH_3)$_2^{2+}$·DN30C10 adducts.[23] Such an interaction is the likely source of the peculiar spectroscopic, photophysical, photochemical, and electrochemical properties of the adducts compared with the properties of the free host and guest components.

In principle, for the aromatic crown ethers an intramolecular interaction between the two aromatic moieties might also take place. No evidence of such an interaction, however, was obtained from the comparison of the absorption and emission spectra of DB30C10 and DN30C10 crowns with those of the respective 1,2-dimethoxy derivatives. Since the DB30C10 and DN30C10 crown ethers are the best candidates to give such an intramolecular interaction because of geometrical reasons, we believe that it can be ruled out in all cases.

Absorption Spectra. The absorption spectra of the aromatic crown ethers show intense bands in the UV region related to π–π^* transitions in the dialkoxybenzene or -naphthalene units.[31] The spectrum of the [Pt(bpy)(NH_3)$_2$](PF_6)$_2$ shows a quite intense absorption in the 290–340-nm region dominated by the bpy-centered π–π^* bands at 308 and 319 nm which hide lower intensity metal-to-ligand (bpy) charge-transfer and metal-centered bands.[22]

The results obtained indicate that in the adducts of Pt(bpy)(NH_3)$_2^{2+}$ with aromatic crown ethers there is an interaction resulting in the decrease in the intensity of the aromatic absorption bands both of the crown ether and of the bpy ligand and the appearance of a new absorption (either as a distinct band or as an intense tail) above 340 nm.

The plots of Figure 4 show that the interaction depends critically on the size of the crown ether ring, as expected from examination of molecular space filling (CPK) models, which show that too small or too large crown rings do not allow a parallel approach of the two aromatic moieties of the crown to the bpy ligand of the platinum complex. A decrease in intensity of π–π^* bands upon perturbation introduced by a face-to-face arrangement of aromatic rings is a well-known phenomenon particularly studied for sandwich dimers and cyclophanes.[32,33] The new absorption band above 340 nm was assigned[22] to a charge-transfer transition from the π-electron-rich dialkoxybenzene or -naphthalene units of the crown ether to the empty π^* orbitals of bipyridine. This assignment is now confirmed (i) by the fact that the band moves to lower energies in the series DB30C10, DN30C10, and BPP34C10, as expected on the basis of the known values[30] of the ionization potentials of the corresponding alkoxy aromatic units, and (ii) by the sensitivity of the band to solvent polarity.

According to Figure 4, the largest perturbation within the homogeneous family of dibenzo crown ethers occurs for DB30C10. This is in agreement with the previous spectroscopic and NMR results[24] and is also consistent with the expectations based on CPK molecular models, which show that DB30C10 has the best size and geometry to host the Pt complex.

Luminescence. The luminescence band with λ_{max} = 453 nm exhibited by Pt(bpy)(NH_3)$_2^{2+}$ in AN solution at 77 K is quite similar to that of other metal-perturbed ligand-centered (LC) phosphorescence bands of complexes containing bpy ligands (see, e.g., Rh(bpy)$_3^{3+}$ [27]). The radiative rate constant (2 × 10^4 s^{-1}),

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[30] (a) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124. (b) Zweig, A.; Maurer, A. H.; Roberts, G. *J. Org. Chem.* **1967**, *32*, 1322.

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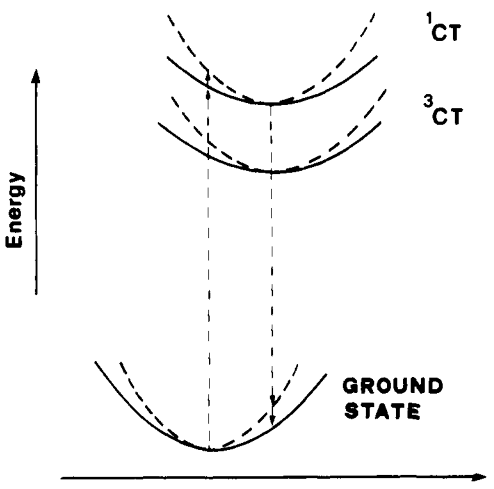

Figure 10. Schematic representation of potential energy curves for ground and charge-transfer excited states in polar (---) and nonpolar solvents (—).

obtained from the experimental lifetime (25 μs) and the luminescence quantum yield (0.5) at 77 K, is in agreement with a ^{3}LC assignment. As the temperature increases, the vibrational structure becomes less pronounced and the relative intensities of the vibronic bands change as it usually happens for other complexes.[8] A strong decrease in the excited-state lifetime can also be observed, suggesting the occurrence of a thermally activated radiationless transition to a short-lived excited state. Association of $Pt(bpy)(NH_3)_2^{2+}$ with the aliphatic 18C6 crown ether does not affect the luminescence properties of the complex.

The adducts with aromatic crowns show, however, a novel broad luminescence band with a maximum in the 550–600-nm region. The energy of the band maximum is solvent dependent, indicating a charge-transfer (CT) orbital origin. We believe that such emission takes place from a triplet CT level related to the electronic transition from the dialkoxybenzene or -naphthalene units of the crown to the bpy ligand of the metal complex, which is also responsible for the broad absorption above 340 nm. The broadness of the absorption and emission CT bands indicates that the equilibrium geometry for ground and excited state is quite different. This is indeed expected because in going from the ground state to a CT excited state (i) the distance between the aromatic rings of the crown and the bpy ring of the metal complex decreases because of electrostatic interaction and (ii) extensive solvent repolarization takes place in the region of the charge separation.

It is noteworthy that the solvent dependence of the CT emission is in the direction opposite from that observed for the CT absorption. A similar behavior has already been observed for MLCT emission and absorption of complexes *fac*-$XRe(CO)_3L$ (X = Cl, Br, I; L = Phpy, bpy)[34] and $(OC)_5W{-}L{-}W(CO)_5$ (L = pyrazine or other bpy-type ligands).[35] The proposed rationalization was based on a different solvent-dependent contraction of the M–L bond in the excited-state relative to the ground-state geometry. A similar scheme might be used for our system, replacing the metal–ligand bond distance with the distance between the aromatic ring(s) of the crown and the bpy ring of the metal. A more likely and more appropriate explanation may be based on the scheme of Figure 10, which depicts the ground- and excited-state potential energy curves as a function of solvent orientation for polar and nonpolar solvents. Because of its 2+ electric charge, the adduct is better solvated by a polar solvent and the solvent reorganization after a vertical CT transition is larger in a polar than in a nonpolar solvent. As one can see from Figure 10, in going from nonpolar to polar solvents a blue shift in absorption and a red shift in emission can thus be expected, in agreement with the experimental result.

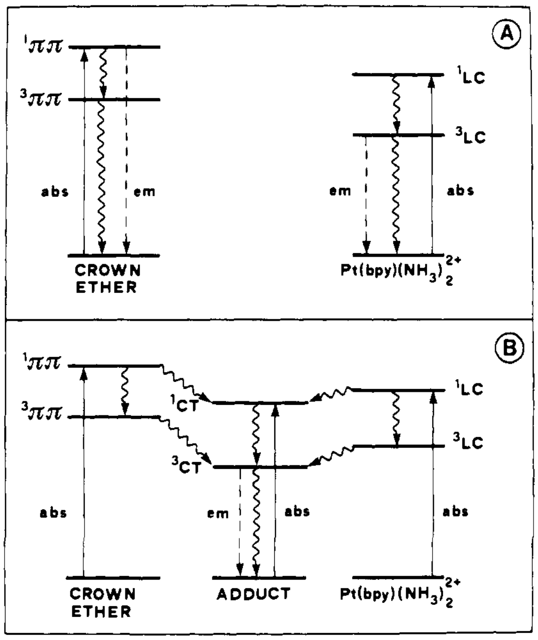

Figure 11. Schematic energy level diagram for the isolated host and guest (A) and for the adduct (B). For more details see text.

As pointed out in the Results, at room temperature the appearance of the broad luminescence band characteristic of the adducts with aromatic crowns is accompanied by the disappearance of the crown fluorescence and the ligand centered $Pt(bpy)(NH_3)_2^{2+}$ phosphorescence. This can be explained on the basis of the schemes shown in Figure 11. When the two components are isolated (Figure 11A), radiative decays of the singlet excited state of the aromatic crown ether and of the triplet LC state of the $Pt(bpy)(NH_3)_2^{2+}$ complex compete with the respective intramolecular radiationless decay processes. In the adduct, however, lower lying CT levels are present, and the excited levels of the crown ether and of the Pt complex apparently undergo fast radiationless decay to such CT levels (Figure 11B). In rigid matrix at 77 K, however, only the crown ether fluorescence is quenched, whereas the ligand-centered $Pt(bpy)(NH_3)_2^{2+}$ phosphorescence is very strong and exhibits a lifetime quite similar to that of the free $Pt(bpy)(NH_3)_2^{2+}$ complex under the same experimental conditions. No adduct emission can be observed under such conditions. These results suggest that at 77 K the adduct is still present (note that the adducts can also be obtained in the solid state)[23,24] but the deactivation of ^{3}LC to ^{3}CT does not take place. There may be two reasons why in rigid matrix at low temperature the $^3\mathrm{LC} \rightsquigarrow {}^3\mathrm{CT}$ deactivation does not occur (i) because of the frozen environment, the ^{3}CT level is not relaxed and may thus lie at higher energy than ^{3}LC and (ii) because the process may require the overcoming of a thermal barrier. The lack of population of the ^{3}CT level at 77 K is supported by the results obtained for the $Pt(bpy)(NH_3)_2^{2+}\cdot DB18C10$ adduct, which exhibits *both* the ^{3}LC phosphorescence *and* the adduct emission in the temperature range 180–298 K. On decreasing temperature (Figure 7) the intensities of both bands increase, but the intensity of the adduct band increases comparatively less than the intensity of the ^{3}LC band, suggesting that the level responsible for the adduct luminescence is populated via a thermally activated process.

Photochemistry. $Pt(bpy)(NH_3)_2^{2+}$ is photoreactive in CH_2Cl_2 when solubilized by the aliphatic 18C6 crown ether. The nature of the photoreaction has not been investigated. As it happens for other Pt(II) complexes in CH_2Cl_2 solution, the process could be a photooxidative addition.[36] Another possibility is a photoreaction involving the bpy ligand as suggested by the decrease of absorbance at 310 nm. No evidence was found for bpy photodissociation. Regardless of the actual nature of the $Pt(bpy)(NH_3)_2^{2+}$ photo-

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(34) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.
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(36) See, e.g.: Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720.

reaction, the important result is that the complex becomes photochemically stable when involved in adducts with the aromatic crown ethers (except DB18C6). This behavior can be explained by an increase in the rate of radiationless decay of the Pt(bpy)$(NH_3)_2^{2+}$ excited states via the CT levels of the adduct and/or by a screening action performed by the host aromatic crown ethers on the guest platinum complex. The lack of quenching of the photoreaction for Pt(bpy)$(NH_3)^{2+}$·DB18C6 is consistent with the presence of the Pt(bpy)$(NH_3)_2^{2+}$ luminescence in this adduct and with the small size of the crown ring, which precludes the formation of a U-shape adduct as shown by CPK molecular models.

Electrochemistry. It is known that the +1 oxidation state of Pt is unstable[37] and that coordinated bpy ligand usually undergoes reversible or quasi-reversible one-electron reduction at a potential less negative than that corresponding to the reduction of free bpy.[38] The Pt$(bpy)_2^{2+}$ complex shows an irreversible reduction wave (assigned as metal centered) at −0.97 V and a partially reversible wave (assigned as ligand centered) at −1.51 V (AN solution, vs SCE).[39] Pt(bpy)$(NH_3)_2^{2+}$ shows an analogous behavior with an irreversible wave at −1.13 V and an almost reversible wave at −1.80 V. For the adduct with DB30C10 in AN solution (where there is an equilibrium with the free components) besides the two above-mentioned waves corresponding to the "free" Pt complex, two other waves were observed at −1.40 and −2.0 V. These waves can be assigned to the metal-centered and ligand-centered reductions of the complex in the adduct. The relative change in intensity of the waves on addition of an excess of host confirms this assignment. In CH_2Cl_2 solution only the adduct is present, and therefore only two reduction waves (concerning the metal and the ligand of the guest complex) are present.

Conclusions. The host–guest adducts obtained from Pt(bpy)$(NH_3)_2^{2+}$ and aromatic crown ethers are interesting and instructive systems for photochemical and photophysical investigations. The two molecular species are kept together by hydrogen bonds between the crown oxygen atoms and the NH_3 ligands of the complex (Figure 9). In addition, there is an electronic interaction between the bpy ligand of the complex and the aromatic rings of the crowns. Such an interaction causes strong changes in the extinction coefficients of the host- and guest-localized bands, the appearance of a CT absorption, the quenching (at room temperature) of the host and guest luminescence, the appearance of a new emission band characteristic of the adduct, and a change in the Pt(II)- and bpy-localized reduction processes. Furthermore, adduct formation protects the guest Pt(bpy)$(NH_3)_2^{2+}$ complex from giving the photoreaction observed for the free Pt(bpy)$(NH_3)_2^{2+}$ complex in CH_2Cl_2 solution. The perturbation effect on the properties of Pt(bpy)$(NH_3)_2^{2+}$ can be tuned by changing the size of the crown ring and the nature and substitution positions of the aromatic rings present in the crown.

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Registry No. [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$, 79953-62-1; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·18C6, 79953-64-3; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·DB18C6, 79953-65-4; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·DB24C8, 79953-66-5; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·DB30C10, 79953-63-2; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·DB36C12, 79953-67-6; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·BMP32C10, 121865-95-0; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·BPP34C12, 121865-96-1; [Pt(bpy)$(NH_3)_2$]$(PF_6)_2$·DN30C10, 111121-42-7.

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Designed Synthesis of a Radical Cation Salt of Ni(tmp): Structural, Magnetic, and Charge-Transport Properties of Bis[(5,10,15,20-tetramethylporphyrinato)nickel(II)] Hexafluorophosphate

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Abstract: Electrochemical oxidation of (5,10,15,20-tetramethylporphyrinato)nickel(II), Ni(tmp), in the presence of hexafluorophosphate ion affords the new molecular conductor $[Ni(tmp)]_2[PF_6]$, which is comprised of partially oxidized $(+^1/_2)$ S_4-ruffled Ni(tmp) molecules stacked metal-over-metal. The PF_6^- anions lie within channels formed by adjacent porphyrin stacks on sites that minimize the porphyrin–hydrogen to –fluorine contacts. The choice of the PF_6^- anion, as being likely to produce an ordered crystal with this degree of partial oxidation, was prompted by an examination of the crystal structures of similar metallomacrocyclic conductors. ESR studies confirm the tmp ligand as the site of oxidation. Single-crystal room-temperature conductivity along the needle (crystallographic *c*) axis averages 75 Ω^{-1} cm^{-1}, somewhat lower than that observed for Ni(tmp)I and for most porphyrinic conductors containing larger porphyrins. The temperature dependence of the conductivity is metallic from room temperature to 205 K and decreases rapidly as the temperature is decreased further. Single-crystal X-ray diffraction measurements at 220 and 150 K demonstrate that this change in behavior does not result from a structural transition at 205 K. The compound crystallizes in space group D_{4h}^4–$P4/nnc$ of the tetragonal system with two formula units in a cell of dimensions a = 16.685 (1) Å and c = 6.994 (1) Å (volume = 1947 $Å^3$) at 220 K. The two Ni(tmp) molecules in the unit cell are separated by 3.497 (1) Å and are rotated with respect to one another by 34.7° (3)°. Full-matrix least-squares refinement of 76 variables gives a final value for the R index on F^2 of 0.127 for 1845 unique observations and a value of 0.045 for the R index on F for the 1243 observations having $F_o^2 > 3\sigma(F_o^2)$.

We have described a series of partially oxidized molecular conductors prepared by chemical oxidation of porphyrinic metallomacrocycles (M(L)) with molecular iodine.[1-6] A single structural motif has been retained throughout this series of ma-