Calixphyrins

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Near-Infrared Emission from Bis-Pt^{II} Complexes of Doubly N-Confused Calix[6]phyrins(1.1.*1*.1.1.*1*)**

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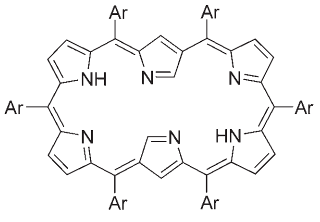
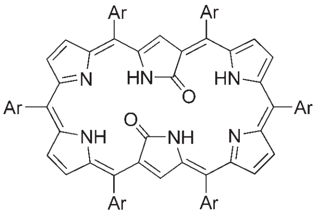
Platinum(II) porphyrins display intense room-temperature phosphorescence with significantly shorter lifetimes than other types of phosphorescent organic compounds,[1–3] which defies the fluorescence–phosphorescence distinction and makes them useful for such applications as oxygen sensing based on phosphorescence quenching[2] and light-emitting devices (LEDs).[3] For potential use in biological systems, however, the light-emitting Pt^{II} complexes should be designed to cover the full visible and near-infrared range (i.e., 650–1100 nm).[4]

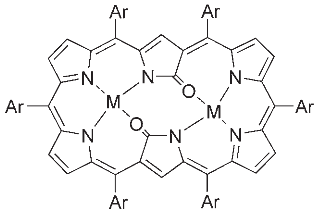
Recently, we reported doubly N-confused hexaphyrin(1.1.1.1.1.1) (N_2C-Hex) that are capable of forming complexes with two metal ions in their rectangular coordination environment consisting of six nitrogen and two carbon atoms (NNNC, NNNC).[5] However, because of the synthetic reason yet unclear and of susceptibility to oxidation, only one type of bis-metal complex of dioxo-substituted hexaphyrin (N_2CO-Hex) bearing an NNNO,NNNO core has been characterized; the emission bands due to the free ligand are observed in the near-infrared (IR) region (> 1050 nm). In an attempt to attain coordination with intact NNNC or NNCC cores, which is expected to bring the emission band close to or within the spectral window of interest, we examined the synthesis of nonconjugated N-confused hexaphyrins and their Pt^{II} metalation. The macrocycles contain two metal coordination cavities consisting of nitrogen and carbon atoms similar to a conjugated one.



N_2C-Hex



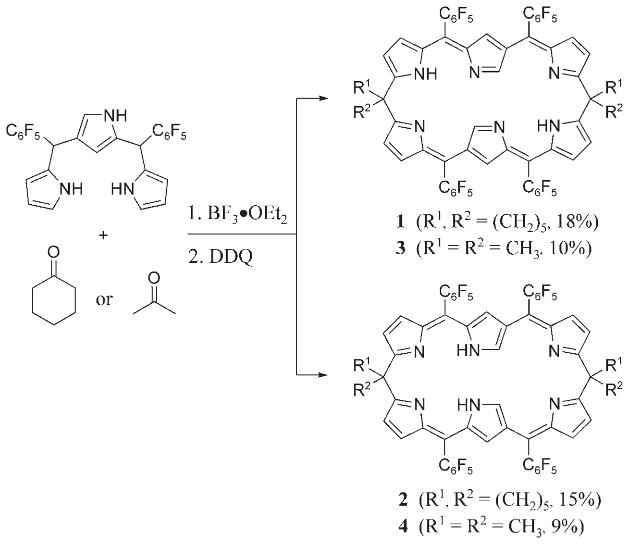
N_2CO-Hex



(M,M)-N_2CO-Hex

Herein, we report the synthesis of doubly N-confused calix[6]phyrins bearing NNNC,NNNC or NNNN,NNCC cores and their bis-Pt^{II} complexes, which exhibit phosphorescence around 1000 nm. These are the first confused expanded porphyrinoids bearing two unsymmetrical coordination cavities that afford stable bis-metal complexes.

The title ligands (**1**–**4**; Scheme 1) were readily synthesized by the condensation of N-confused tripyrrane[5a] with excess cyclohexanone or acetone in the presence of acid catalyst and subsequent oxidation.[6] According to the condensation manner of N-confused tripyrrane (either head-to-tail or head-to-head), two types of macrocycles with different



Scheme 1. Synthesis of doubly N-confused calix[6]phyrins(1.1.*1*.1.1.*1*).

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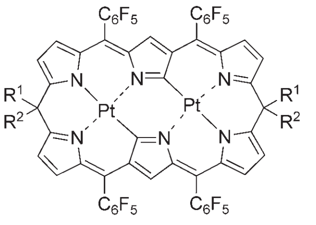
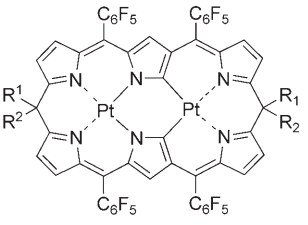
coordination modes (NNNC,NNNC or NNNN,NNCC) were formed. Because the two macrocycles have the same molecular symmetry, their ^{1}H NMR spectra were very similar. For example, in the spectra of **1** (and **2**) in $CDCl_3$, one singlet signal ascribable to NH protons was seen at $\delta = 13.53$ (13.58) ppm and two singlet signals due to α-CH and β-CH protons of the confused pyrrole ring were observed at $\delta = 10.28$ (9.94) and 6.03 (5.83) ppm, respectively. Therefore, conclusive assignment of the structures for **1** and **2** as shown in Scheme 1 was based on X-ray single-crystal analysis (see below) together with the theoretical calculations on each tautomeric form.[7] The new macrocycles are very stable and the α positions of the confused pyrrole rings remain intact in solution under air, which is in a marked contrast to the conjugated doubly N-confused hexaphyrin(1.1.1.1.1.1), which affords the dioxo derivative readily.[5a]

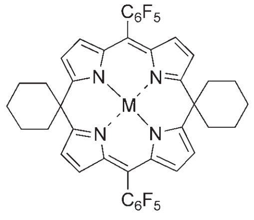
The corresponding Pt^{II} complexes were prepared in good yields by treating **1**–**4** with $[PtCl_2(NCPh)_2]$ in benzonitrile at 130 °C.[1c,8] For comparison, a Pt^{II} complex of calix[4]phyrin (**5**)[6] was also synthesized (Figure 1). The coordination of two Pt^{II} metals in the cavities of calix[6]phyrins was indicated by the absence of NH protons and the α-CH protons of the confused pyrroles in the ^{1}H NMR spectra. Interestingly, in the reactions of **1** and **4**, mono-Pt^{II} complexes were separated as side products; however, similar mono-Pt^{II} complexes were not isolated in the reactions of **2** and **3**. The metalation site of mono-Pt complex **1**-Pt was determined by the characteristic ^{1}H NMR signals, one for NH proton and the other for α-CH proton of the confused pyrrole ring. In the case of mono-Pt complex of **4** (**4**-Pt), the Pt metal is captured only in the NNCC core, as judged from the ^{1}H NMR spectrum, in which the signal of two α-CH protons of the confused pyrrole rings disappears while the signal of NH protons remains.



1-Pt-Pt (R^1, R^2 = $(CH_2)_5$, 65%)
3-Pt-Pt (R^1 = R^2 = CH_3, 37%)



2-Pt-Pt (R^1, R^2 = $(CH_2)_5$, 57%)
4-Pt-Pt (R^1 = R^2 = CH_3, 24%)



5 (M = H_2)
5-Pt (M = Pt, 84%)

Figure 1. Bis-Pt^{II} complexes of doubly N-confused calix[6]phyrins (**1**–**4**) and Pt^{II} complex for calix[4]phyrin (**5**).

The explicit structural assignment, especially on the configurations of the confused pyrrole rings for the two isomers, came from the X-ray single-crystal diffraction analyses of free bases **3** and **4** and their Pt^{II} complexes (Figure 2).[9] For **3** and **4**, the arrangement of the confused pyrrole rings was verified to be NNNC,NNNC for **3** and NNNN,NNCC for **4**. Both macrocycles adopt a rooflike (Λ-shaped) conformation bending along the axis defined by the two sp^3-hybridized *meso*-carbon atoms. The roof angles of **3** and **4** are 103.8° and 104.7°, respectively. In contrast, **3**-Pt-Pt and **4**-Pt-Pt display ruffled molecular structures. The distances between two Pt metals are 3.86 and 3.88 Å, respectively. Direct interactions between the Pt metals are, thus, not expected.

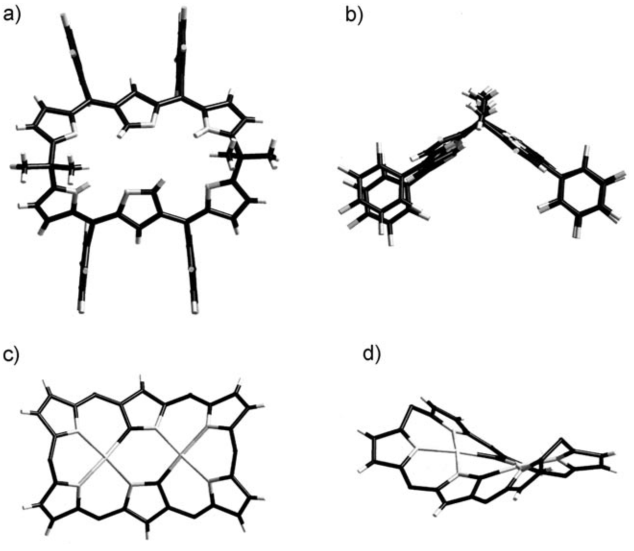


Figure 2. X-ray crystal structures of **3** and **3**-Pt-Pt: a) top view and b) side view of **3**; c) top view and d) perspective view of **3**-Pt-Pt. (Pentafluorophenyl and methyl groups are omitted for clarity in (c) and (d).)

The absorption spectra of **3** and **4** are slightly different, showing split absorption maxima at 505 and 530 nm for **3**, but just one broad peak for **4** in toluene. The corresponding bis-Pt^{II} complexes, however, show a similar absorption profile (Figure 3).

No emission was detected from free ligands **1**–**4** and calix[4]phyrin (**5**), whereas their Pt^{II} complexes were found to display light-emitting properties in the near-IR region at room temperature as shown in Figure 3 c,d and Table 1. Emission bands of Pt^{II} calix[n]phyrins ($n = 4$ and 6) in toluene were observed around 850 and 1000 nm, respectively, showing large Stokes shifts relative to those of Pt^{II} porphyrins (ca. 3100 cm^{-1}).[1] When the solution was deoxygenated by argon bubbling, the emission intensities and the quantum efficiencies of Pt^{II} complexes were found to increase while the 1270 nm emission band due to singlet oxygen was diminished, indicating the relaxation pathway involving energy transfer down to the oxygen molecule from the higher-lying excited triplet state of the Pt^{II} complexes. Among the bis-Pt^{II} complexes, **4**-Pt-Pt exhibits much stronger emission and

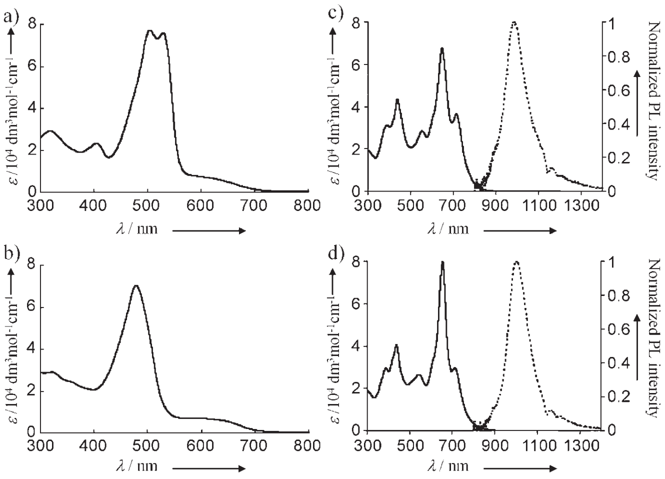


Figure 3. Absorption (solid line) and emission (doted line, $\lambda_{ex} = 610$ nm) spectra of a) **3**, b) **4**, c) **3**-Pt-Pt, and d) **4**-Pt-Pt in toluene at 298 K.

Table 1: Photophysical properties for Pt^{II} calix[*n*]phyrins (*n* = 4 and 6).

Compound	λ_{abs} [nm]	λ_{em}[a] [nm]	Φ_{PL}[b]	τ[c] [ns]	Stokes shift [cm^{-1}]
1-Pt-Pt	649, 725	1010	6.8×10^{-4}	29.6	3892
2-Pt-Pt	657, 722	1029	1.2×10^{-3}	20.1	4132
3-Pt-Pt	649, 716	986	1.8×10^{-3}	39.2	3824
4-Pt-Pt	654, 713	1003	2.7×10^{-3}	25.5	4055
5-Pt	446, 546	854, 891[d]	1.3×10^{-2}	1040	6605

[a] $\lambda_{ex} = 610$ nm ($A = 0.1$) in toluene. [b] Photoluminescence quantum yield; IR1040 ($\Phi_{PL} = 0.012$)[10] used as a standard. [c] Measured in CH_2Cl_2. [d] $\lambda_{ex} = 590$ nm.

efficient quantum yields, whereas **1**-Pt-Pt shows lower quantum efficiency. Substitution of cyclohexyl groups at the *meso*-position of bis-Pt^{II} complexes resulted in a red shift by around 25 nm of the emission peak relative to those of the ligand with methyl groups. The configuration of the cores was also found to affect the emission properties. In fact, the emission peaks of the bis-Pt^{II} complexes (**2**-Pt-Pt or **4**-Pt-Pt) bearing two different coordination environments were red-shifted by around 20 nm relative to those of the symmetric counterparts (**1**-Pt-Pt or **3**-Pt-Pt).

Interestingly, configurational changes were even manifest in the dynamic emission properties, and a clear correlation was observed between decay lifetimes and the different classes of cores. Consistently longer lifetimes were obtained for compounds with symmetric cores (**1-Pt-Pt** and **3-Pt-Pt**; NNNC,NNNC) than for their unsymmetrical counterparts. The switch of substituents from cyclohexyl to methyl groups also brought an extension of lifetime. The emission lifetimes of bis-Pt^{II} complexes are much shorter than that of monometallic **5**-Pt, which is probably due to the presence of two heavy atoms and the small energy gaps involved in the energy relaxation in the bis-Pt^{II} complexes.

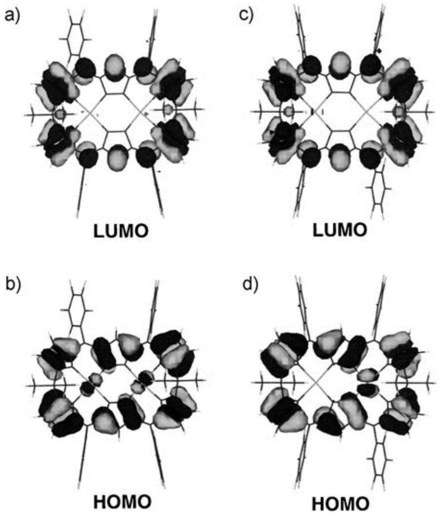


Figure 4. Kohn–Sham orbitals of a) LUMO and b) HOMO of **3**-Pt-Pt, and c) LUMO and d) HOMO of **4**-Pt-Pt.

Figure 4 shows the Kohn–Sham orbitals of **3**-Pt-Pt and **4**-Pt-Pt calculated at the B3LYP/631 LAN level[11] in an attempt to give an account for the short lifetimes as observed for the unsymmetrical derivatives. The d orbitals of the two metal atoms in the core contribute equally to the HOMO of **3**-Pt-Pt, whereas only one of the two metal atoms corresponding to the NNCC core contributes the d orbital to the HOMO of **4**-Pt-Pt. Importantly, almost no d-orbital contribution from the metal atoms to the LUMO is observed for either complex. Accordingly, symmetry considerations mean that **3**-Pt-Pt has only a vanishingly small transition dipole moment for the HOMO–LUMO transition, whereas **4**-Pt-Pt has a significant transition dipole moment, which is expected to allow the quick release of energy during the relaxation processes.

Cyclic-voltammetry measurements on bis-Pt^{II} calix[6]phyrins revealed the two reversible oxidation steps and the two reversible reductions peaks (Table 2). The redox potentials and consequently the electrochemical HOMO–LUMO band gaps for all bis-Pt^{II} complexes show nearly the same values of approximately 1.65 V, which indicates that the redox processes take place at the π-ligand moieties and that the effect of the coordination environment is modest.

Table 2: Cyclic voltammetry [*E*/V vs. ferrocene/ferrocenium] of bis-Pt^{II} complexes in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at a Pt working electrode.

Compound	$E_{ox,2}$	$E_{ox,1}$	$E_{red,1}$	$E_{red,2}$	$\Delta E^{\circ}_{1/2}$[a]
1-Pt-Pt	0.89	0.56	−1.09	−1.35	1.65
2-Pt-Pt	0.88	0.53	−1.10	−1.37	1.63
3-Pt-Pt	0.87	0.55	−1.12	−1.32	1.67
4-Pt-Pt	0.90	0.53	−1.12[b]	−1.32[b]	1.65

[a] Potential difference between the first oxidation and first reduction processes. [b] Pseudoreversible.

In summary, we have synthesized new types of doubly N-confused calix[6]phyrins (**1**–**4**) and their Pt^{II} complexes. The bis-Pt^{II} calix[6]phyrins displayed phosphorescence as opposed to fluorescence in the near-IR region around 1000 nm with shorter-than-expected lifetimes at room temperature. The bis-Pt^{II} calix[6]phyrins as well as monometallic Pt^{II} calix[4]phyrin, because of their facile synthesis and the near-IR emission properties that can be tailored at wavelengths longer than those of conventional Pt^{II} complexes, hold promise as a new class of IR luminescent dye.

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Keywords: calix[*n*]phyrins · luminescence · phosphorescence · platinum

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[9] Crystal data: **3**, red plate, $C_{58}H_{26}F_{20}N_6 \cdot CH_2Cl_2$, $M_r = 1271.78$, orthorhombic, space group $Pca2_1$ (No. 29), $a = 26.6347(8)$, $b = 19.3562(6)$, $c = 10.2527(3)$ Å, $V = 5285.7(3)$ Å^3, $Z = 4$, $T = 150(2)$ K, $R = 0.0634$ ($I > 2\sigma(I)$), $R_w = 0.1768$, GOF = 1.096; **3**-Pt-Pt, dark purple block, $2(C_{58}H_{22}F_{20}N_6Pt_2) \cdot 2(C_7H_{16})$, $M_r = 1673.18$, monoclinic, space group $P2_1$ (No. 4), $a = 12.1513(11)$, $b = 32.734(3)$, $c = 15.2684(14)$ Å, $\beta = 103.044(1)°$, $V = 5916.5(9)$ Å^3, $Z = 2$, $T = 123(2)$ K, $R = 0.0625$ ($I > 2\sigma(I)$), $R_w = 0.1150$, GOF = 1.002. Crystallographic data for **4**, **4**-Pt-Pt, and **5** are summarized in the Supporting Information. CCDC 682904 (**3**), 682905 (**4**), 682906 (**3**-Pt-Pt), 682907 (**4**-Pt-Pt), and 682908 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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