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The Synthesis and Characterization of a Group of Transition Metal Octabutoxynaphthalocyanines and the Absorption and Emission Properties of the Co, Rh, Ir, Ni, Pd and Pt Members of This Group

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Abstract

The synthesis and photophysical properties of new metallo-octabutoxynaphthalocyanines with Rh(III), Ir(III), and Pt(II) are reported. Various metals were inserted into the metal-free octabutoxynaphthalocyanine and the resultant metal complexes were fully characterized by NMR, UV-vis spectroscopy, and mass spectrometry.

The absorption and emission properties of these new complexes were also examined and compared to those of Co(II), Ni(II), and Pd(II) octabutoxynaphthalocyanines. The results provide useful information to understand the effect of these transition metals on the properties of this macrocyclic ring.

Keywords

metal insertion; absorbance; quantum yield; phosphorescence; fluorescence; Q-band

1. Introduction

Naphthalocyanines (Ncs), with four additional benzene rings to the phthalocyanine, are very stable macrocycles with an intense absorption in the red to deep red region (so-called Q band). However, these highly conjugated compounds generally have low solubility, which limits their application. Previously, it has been shown that the addition of alkoxy substituents on the non-peripheral positions of the ring not only increases the solubility but also shifts the Q-band further into the near-IR region, making these compounds attractive candidates for optical data storage devices, photovoltaics, and as therapeutic agents [1, 2].

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Metals can be coordinated into the macrocycle cavity, providing another mean to further modify physical and chemical properties of the macrocycle [3, 4]. Since metal-free octabutoxynaphthalocyanine ($\text{H}_2\text{Nc}(\text{OBu})_8$) and the Cu complex of the pentyloxy analogue were first synthesized by Cook et al. [5], different metal complexes of $\text{Nc}(\text{OBu})_8$ have been synthesized and investigated for their photochemical properties [6–8] and for their application in various fields [9–14]. However, the metal complexes studied thus far have mostly been limited to the first row transition metal complexes. Although the synthesis of Ru and Os $\text{Nc}(\text{OBu})_8$ complexes was reported recently [15], only $\text{PdNc}(\text{OBu})_8$ has been studied for its photophysical and photochemical properties from the second and third row transition metals [10, 11].

In the current study, we synthesized new metal complexes of $\text{Nc}(\text{OBu})_8$ with Rh(III), Ir(III), and Pt(II) by inserting these metals into the free-base compound, Figure 1. Insertion reactions with these metals were accompanied with significant decomposition of the reactant. However, the obtained metal complexes of $\text{Nc}(\text{OBu})_8$ were stable and characterized by ^1H -NMR, UV-vis spectroscopy, and mass spectrometry's. The emission spectra of these new complexes were also examined. The properties of the newly synthesized complexes were compared with the Co(II), Ni(II), and Pd(II) complexes.

2. Material and methods

2.1. Materials

$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, PdCl_2 , bis(1,5-cyclooctadiene)diiridium(I) dichloride ($[\text{Ir}(\text{C}_8\text{H}_{12})\text{Cl}]_2$), and PtCl_2 and solvents for the spectroscopic measurements, toluene (99.5%, spectrophotometric grade) and benzene (99%, HPLC grade), were purchased from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous solvents used for synthesis were purchased from Fisher Sci. (Pittsburgh, PA, USA). $\text{H}_2\text{Nc}(\text{OBu})_8$ was synthesized according to the literature procedure [10].

2.2. Characterization

^1H -NMR spectra were recorded in CDCl_3 on a Varian Gemini 300 spectrometer. Chemical shifts are given in ppm relative to CHCl_3 (7.26 ppm). The high resolution ESI-TOF spectra were obtained from Washington University Resource for Biomedical and Bio-organic Mass Spectrometry. All measured masses of the metal complexes fall within ± 5 ppm of calculated values. The ground state electronic absorption spectra were recorded on a Varian Cary 50 Bio UV-visible single beam spectrophotometer (Varian Corporation) at a resolution ± 1 nm using a 10 mm path length quartz cuvette. Toluene was used as a solvent. The photophysics of the Rh complex were measured in benzene containing pyridine (1%, by volume) in order to prevent ligand loss.

Steady-state near-IR luminescence spectra were obtained at room temperature in Ar-saturated benzene on a PTI Instruments QM-4/2006-SE spectrofluorimeter. Samples in a 10 mm $\times$ 10 mm path length quartz cuvette were excited using a 75 W Xe Arc lamp excitation source, and near-IR signals were monitored at the right-angle geometry using a Peltier cooled InGaAs detector with lock-in amplification. Appropriate filters were used to avoid scattered light from entering the detection system. All spectra were corrected for the sensitivity of the detector.

Phosphorescence emission was measured using Xe arc excitation (800–810 nm) at a concentration of $\sim 6 \mu\text{M}$, yielding an optical absorbance of ~ 1.2 a.u. in the Q band maximum.

2.3. Fluorescence quantum yield measurements

Fluorescence quantum efficiencies were measured using $\text{ZnNc}(\text{OBu})_8$ in benzene as a standard. The reference and the samples were excited at 458 nm where they had the same absorbance ($A \approx 0.02$ a.u.). The areas under the fluorescence spectra (G) were measured and fluorescence quantum efficiencies (q_M) were obtained from the equation:

$$q_M^{\text{MNC}(\text{OBu})_8} = \frac{G_{\text{MNC}(\text{OBu})_8}}{A_{\text{MNC}(\text{OBu})_8}} \times \frac{A_{\text{ZnNc}(\text{OBu})_8}}{G_{\text{ZnNc}(\text{OBu})_8}} \times q_M^{\text{ZnNc}(\text{OBu})_8}$$

The value for the absolute fluorescence quantum efficiency for the Zn complex was estimated using the Strickler-Berg equation [16]:

$$\frac{1}{\tau_{\text{rad}}} = k_{\text{rad}} = 2.88 \cdot 10^{-9} \times \frac{n_f^3}{n_a} \times (\nu_f^{-3})^{-1} \times \int \frac{\epsilon d\nu}{\nu}$$

The calculated radiative lifetime was 8.45 ns, in good agreement with the value for unsubstituted ZnNc measured in DMF (8.8 ns) [17]. Singlet state lifetime was measured by the transient absorption spectrometry of 0.6 ns and used to calculate the absolute quantum efficiency of the Zn complex of $q_M = 0.07$.

2.4. Synthesis

2.4.1. Preparation of $\text{CoNc}(\text{OBu})_8$ — $\text{CoNc}(\text{OBu})_8$ was synthesized according to the literature and obtained with 78% yield [7]. UV-vis (toluene) λ_{max} , nm (log ϵ): 832 (5.2). HRMS-ESI-TOF m/z : $[\text{M}]^+$ calcd for $\text{C}_{80}\text{H}_{88}\text{N}_8\text{O}_8^{59}\text{Co}$, 1347.6057; found, 1347.6029. The compound is a green solid. It is soluble in CH_2Cl_2 , dimethylformamide and toluene, and slightly soluble in hexanes.

2.4.2. Preparation of $\text{NiNc}(\text{OBu})_8$ — $\text{NiNc}(\text{OBu})_8$ was synthesized according to the literature and obtained with 65% yield [6]. UV-vis (toluene) λ_{max} , nm (log ϵ): 844 (5.4). ^1H NMR (δ , 300 MHz, CDCl_3 , 25°C): 8.90 (m, 8H, 1,4-Nc H), 7.84 (m, 8H, 2,3-Nc H), 5.01 (t, 16H, OCH_2), 2.18 (m, 16H, OCH_2CH_2), 1.63 (m, 16H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.01 (t, 24H, $\text{OC}_3\text{H}_6\text{CH}_3$) ppm. The compound is a green solid. It is soluble in CH_2Cl_2 , dimethylformamide and toluene, and slightly soluble in hexanes.

2.4.3. Preparation of $\text{RhNc}(\text{OBu})_8\text{Cl}(\text{py})$ —Under Ar, a mixture of $\text{H}_2\text{Nc}(\text{OBu})_8$ (170 mg, 0.132 mmol) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (154 mg, 0.396 mmol) in pyridine (10 mL) was refluxed for 2 days and evaporated to dryness by rotary evaporation (room temperature). The solid was washed with a solution of CH_3OH and H_2O (1:1, 10 mL), chromatographed (Al_2O_3 III, toluene-hexanes 2:1), vacuum dried (room temperature), and weighed (70 mg, 0.046 mmol, 35%). UV-vis (toluene) λ_{max} , nm (log ϵ): 819 (5.2). ^1H NMR (δ , 300 MHz, CDCl_3 , 25°C): 8.94 (m, 8H, 1,4-Nc H), 7.86 (m, 8H, 2,3-Nc H), 6.51 (m, 1H, 4-py H), 5.72 (m, 2H, 3,5-py H), 5.26 (t, 16H, OCH_2), 3.19 (m, 2H, 2,6-py H), 2.25 (m, 16H, OCH_2CH_2), 1.69 (m, 16H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.06 (t, 24H, $\text{OC}_3\text{H}_6\text{CH}_3$) ppm. HRMS-ESI-TOF m/z : $[\text{M}]^+$ calcd for $\text{C}_{85}\text{H}_{93}^{35}\text{ClN}_9\text{O}_8^{103}\text{Rh}$, 1506.5923; found, 1506.5942. The complex is a brown-green solid. It is soluble in CH_2Cl_2 , dimethylformamide and toluene, and slightly soluble in hexanes.

2.4.4. Preparation of $\text{PdNc}(\text{OBu})_8$ — $\text{PdNc}(\text{OBu})_8$ was synthesized according to the literature but PdCl_2 was used as metal source [10]. The Pd complex was obtained with 65%

yield. UV-vis (toluene) λ_{max} , nm (log ϵ): 827 (5.4). ^1H NMR (δ , 300 MHz, CDCl_3 , 25°C): 8.95 (m, 8H, 1,4-Nc H), 7.87 (m, 8H, 2,3-Nc H), 5.19 (t, 16H, OCH_2), 2.24 (m, 16H, OCH_2CH_2), 1.66 (m, 16H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.03 (t, 24H, $\text{OC}_3\text{H}_6\text{CH}_3$) ppm. The complex is a brown-green solid. It is soluble in CH_2Cl_2 , dimethylformamide and toluene, and slightly soluble in hexanes.

2.4.5. Preparation of $\text{IrNc}(\text{OBu})_8\text{Cl}(\text{py})$ —Under Ar, a mixture of $\text{H}_2\text{Nc}(\text{OBu})_8$ (290 mg, 0.225 mmol) and bis(1,5-cyclooctadiene)diiridium(I) dichloride (452 mg, 0.674 mmol) in pyridine (15 mL) was refluxed for 3 days and evaporated to dryness by rotary evaporation (room temperature). The solid was washed (CH_3OH), chromatographed (Al_2O_3 III, toluene-hexanes 2:1), vacuum dried (room temperature), and weighed (70 mg, 0.044 mmol, 19%). UV-vis (toluene): λ_{max} , nm (log ϵ): 802 nm (5.5). ^1H NMR (δ , 300 MHz, CDCl_3 , 25°C): 8.91 (m, 8H, 1,4-Nc H), 7.84 (m, 8H, 2,3-Nc H), 6.50 (m, 4-py H), 5.68 (m, 3,5-py H), 5.23 (t, 16H, OCH_2), 3.17 (m, 2,6-py H), 2.23 (m, 16H, OCH_2CH_2), 1.68 (m, 16H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.04 (t, 24H, $\text{OC}_3\text{H}_6\text{CH}_3$) ppm. HRMS-ESI-TOF m/z : $[\text{M}]^+$ calcd for $\text{C}_{85}\text{H}_{93}^{35}\text{ClIrN}_9\text{O}_8^{193}\text{Ir}$, 1595.6466; found, 1595.6442. The complex is a green solid. It is soluble in CH_2Cl_2 , dimethylformamide and toluene, and slightly soluble in hexanes.

2.4.6. Preparation of $\text{PtNc}(\text{OBu})_8$ —Under Ar, a heated (60 °C) solution of $\text{H}_2\text{Nc}(\text{OBu})_8$ (36 mg, 0.028 mmol), 2,6-di-tert-butylpyridine (0.01 mL, 0.04 mmol) in tetrahydrofuran (5 mL) was treated with 10 portions of PtCl_2 (54 mg total, 0.20 mmol) over 4 days. The reaction mixture was filtered and evaporated to dryness by rotary evaporation (room temperature). The solid was chromatographed (Al_2O_3 III, toluene), washed (hexanes), vacuum dried (room temperature), and weighed (8.0 mg, 0.0054 mmol, 19%). UV-vis (toluene): λ_{max} , nm (log ϵ): 811 nm (5.4). ^1H NMR (δ , 300 MHz, CDCl_3 , 25°C): 8.93 (m, 8H, 1,4-Nc H), 7.87 (m, 8H, 2,3-Nc H), 5.18 (t, 16H, OCH_2), 2.24 (m, 16H, OCH_2CH_2), 1.66 (m, 16H, $\text{OC}_2\text{H}_4\text{CH}_2$), 1.03 (t, 24H, $\text{OC}_3\text{H}_6\text{CH}_3$) ppm. HRMS-ESI-TOF m/z : $[\text{M}]^+$ calcd for $\text{C}_{80}\text{H}_{88}\text{N}_8\text{O}_8^{195}\text{Pt}$, 1483.6378; found, 1483.6337. The complex is a brown-green solid. It is soluble in CH_2Cl_2 , dimethylformamide and toluene, and slightly soluble in hexanes.

3. Results and Discussion

3.1. Synthesis

The reactions used to prepare the complexes are given in Scheme 1. Insertion reactions were monitored by following the Q-band in the UV-vis spectrum and continued until the Q-band of the reactant (865 nm) completely disappeared. After purification, each complex was tested by UV-vis in a concentrated solution (over 0.5 au); an absence of the band at ~865 nm confirmed that no metal free reactant interfered with our experiments. No attempt was made to optimize reaction conditions to increase products yields, except for the Pt complex.

An interesting feature found for the insertion reaction with Rh, Ir, and Pt was that the insertion reaction was achieved only with the reported metal sources under the given conditions. Rh and Ir complexes were prepared by refluxing the metal-free compound with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ or $[\text{Ir}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ in pyridine. The slow insertion reaction was accompanied by the decomposition of the reactant, which was monitored by the decrease in the Q-band. Other metal sources, such as Rh(III) chloride or Ir(III) chloride, did not yield any observable metal complexes.

For the Pt complex, 9 equivalent PtCl_2 and metal-free $\text{Nc}(\text{OBu})_8$ were heated (60°C) in tetrahydrofuran for 4 days. Increasing reaction temperature in different solvents accelerated decomposition, whereas reaction at lower temperature did not produce any macrocycle products. Therefore, the Pt insertion reaction was optimized to increase the ratio of insertion/

decomposition. Another difficulty found with the Pt insertion was that the condition found for the reaction only worked for a small scale (~40 mg of starting material). Attempted scale-up of the synthesis significantly decreased the reaction yield.

As described above, decomposition of the reactant caused significantly lower yields for Rh-, Ir-, and PtNc(OBu)₈ compared to first row transition metals. It is possible that these two competing reactions, decomposition and metal insertion, shared the same highly unstable transition state. This speculation was based on the fact that no decomposition of the reactant was observed in the presence of metal sources that did not give any product.

3.2. ¹H-NMR spectrum

Except for Co(II), the metals in these complexes have either strong field octahedral d⁶ (Rh(III) and Ir(III)) or strong field square planar d⁸ (Ni(II), Pd(II), and Pt(II)) configurations and gave clear NMR spectroscopic signals. ¹H-NMR chemical shifts of the metal-free and the metallo-Nc(OBu)₈ are summarized in Table 1. The NMR resonances of the complexes are as expected; the 1,4 and 2,3 resonances of the naphthalocyanine ring appearing at ~8.9 and ~7.9, and the alpha, beta, gamma, and delta resonances of the butoxy substituents appearing at ~5.2, ~2.2, ~1.7 and ~1.0, respectively. The proton resonances of the pyridine ligand of the Rh and Ir complexes are shifted upfield by the ring current effect.

3.3. Ground state absorption spectra

The normalized ground state absorption spectra of the Ni, Pd, Pt, Co, Rh, and Ir complexes in toluene are shown in Figure 2. The spectra of the Ni, Co, and Pd complexes are consistent with those reported in the literatures [6, 7, 10]. The absorption spectra of the investigated series are all dominated by the Q(0,0) band in the 800–845 nm region, corresponding to the transition to the lowest (π, π^*) electronically excited state. The overlapping band to the blue arises from macrocyclic vibrations. Besides the near-IR Q band, the spectra also show a weaker Soret band at ~310 nm, deriving from excitation to the next higher (π, π^*) excited state. In addition, they show a band near 450 nm, which is attributed to the butoxy substituents as suggested by previous theoretical studies on the phthalocyanines NiPc(OBu)₈ and NiPc [18]. The presence of axial ligands in the Rh and Ir complexes does not significantly perturb the common features of the absorption spectra.

The extinction coefficients at the Q-band maxima, ϵ_Q , for the Ni, Pd, Pt and Ir complexes are $\sim 2.6 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ while those for the Co and Rh complexes are considerably lower (Table 2). Beer-Lambert law plots are linear between 1–100 μM and thus show no evidence for aggregation of the complexes.

The Q band shifts to the blue with increasing atomic number in the Ni, Pd, Pt and the Co, Rh, Ir sets of complexes. It also shifts to the blue in the Rh and Ir complexes compared to the Pd and Pt complexes, respectively. These shifts are attributed to an increase in the π -back donation from the metal to the macrocycle LUMO, associated with a progressive increase of the radius of the metal. The increase in the π -back bonding should destabilize the macrocycle-derived LUMO as previously reported [19, 20]. This destabilization of the LUMO increases the HOMO-LUMO energy gap causing the observed red-shifts. Another possible contributor to the blue shifts is the stretching of the macrocycle that occurs as the radius of the metal increases. This stretching reduces the antibonding interactions between the 2pz orbitals of adjacent pyrrole carbon atoms in the macrocycle, and it stabilizes the macrocycle HOMO resulting in the increase in the HOMO-LUMO energy gap.

3.4. Emission spectra

The ground state absorption spectra in the Q band region and the fluorescence emission spectra for the Pd, Pt, Rh, and Ir complexes are shown in Figure 3. The emission spectrum of the Pd compound is consistent with the previous report [10]. Also shown in Figure 3 are phosphorescence emission spectra measured in Ar-saturated benzene at room temperature. In aerated solutions, all compounds exhibited a luminescence signal with $\lambda_{\text{max}} = 1250$ nm. This has been reported earlier for the Pd compound and assigned to the emission arising from the $^1\Delta_g \rightarrow ^3\Sigma_g$ transition in oxygen, generated by energy transfer from triplet state precursors. Based on the phosphorescence maxima from Figure 3, the energy transfer from the T_1 state to molecular oxygen for the Pd and Rh complexes is strictly endergonic.

Figure 3 shows an interesting trend in the position of the fluorescence emission maxima; Stokes shifts of the Pt and Ir complexes are greater than those of the Pd and Rh complexes (Table 2). The same trend is observed also in the Pd and Pt complexes in benzene (Stokes shift is 1145 cm^{-1} in the Pt complex vs. 226 cm^{-1} in the Pd complex) [21]. This large Stokes shift can be attributed to changes in the S_1 excited state geometry of the Pt and Ir complexes. As mentioned earlier, in the Pt and Ir complexes, the π -backbonding contribution from the metal d_{π} orbitals to the macrocycle LUMO is increased compared to their Pd and Rh analogues [22]. The larger metal contribution into the LUMO most likely causes the larger displacement along the M-N_p (pyrrolic nitrogen) coordinate of the complexes in the excited state, resulting in greater changes in the excited state geometry. Alternatively, the large Stokes shift might be an admixture of the triplet state character into the excited singlet state of the Pt and Ir complexes.

Table 2 also lists the fluorescence quantum efficiencies of the complexes measured using the ZnNc(OBu)₈ as a standard. An approximate value for the absolute quantum efficiency of the Zn complex was estimated using the Strickler-Berg equation to calculate the radiative lifetime of the Zn complex ($\tau_{\text{FM}} = 8.45\text{ ns}$) [16] and dividing this into the measured singlet state lifetime ($\tau_{\text{M}} = 0.6\text{ ns}$) of the same complex [22]. The resulting absolute quantum efficiency for ZnNc(OBu)₈ is 0.07. The Pt and Ir complexes are ca. 30% less efficient than their second row metal analogues. It is expected because of an increased spin-orbit coupling that enhances the intersystem crossing process. For the same reason, the Rh and Ir complexes are less fluorescent, compared to the Pd and Pt complexes. Consequently, the phosphorescence is more efficient in the Pt and Ir complexes.

The reported absorption and emission properties of the Rh, Pd, Ir, and PtNc(OBu)₈ complexes correlate well with the effect of increasing the atomic number of the transition metal coordinated in the naphthalocyanine cavity within both groups and periods in the periodic table. The emission properties of these new naphthalocyanine complexes with heavy transition metals indicate that these complexes are attractive candidates for application as oxygen sensing probes, since their triplet state energies are sufficiently close to that of the singlet oxygen. This close triplet state energies between the molecules may allow reversible energy transfer from O₂ back to the macrocycle's T_1 state, which phosphoresces with higher quantum efficiency than singlet oxygen alone [10, 23–26].

4. Conclusions

We reported the synthesis of MNc(OBu)₈ where M is Rh, Ir, or Pt. Reaction yields with these metals were significantly decreased compared to the complexes with first row transition metals. The resultant metal complexes were characterized by ¹H-NMR, UV-vis spectroscopy, mass spectrometry, and emission spectrometry. Comparison of the photophysical properties of the Rh, Pd, Ir, and Pt complexes allowed an examination of the effect of increasing the atomic number of the transition metal coordinated in the tetrapyrrole cavity

within both groups and periods in the periodic table. These new series of metal complexes provided useful information to understand the effect of the incorporated heavy transition metals on the properties of the naphthalocyanine macrocycle.

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Abbreviations

Nc	Naphthalocyanine
Pc	phthalocyanine

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Figure 1.
Structure and proton labelling scheme of $\text{Mn}(\text{OBu})_8$.

Figure 2. Normalized ground state absorption spectra of Co-, Rh- and IrNc(OBu)₈ (A) and Ni-, Pd- and PtNc(OBu)₈ (B) series taken in toluene.

Figure 3.

Absorption spectra in the Q band maxima (gray lines), and fluorescence and phosphorescence emission spectra (black lines) of Rh- and IrNc(OBu)₈ (A) and Pd- and PtNc(OBu)₈ (B) series in benzene at 22°C. The fluorescence spectra were obtained in Ar-saturated benzene with 458 nm excitation. The phosphorescence spectra were obtained with Ar-saturated solutions using 458 nm excitation for the Pt- and Ir complexes, and $\lambda_{\text{exc}} = 800$ nm and $\lambda_{\text{exc}} = 810$ nm for the Pd- and Rh complexes, respectively.

Scheme 1.

The synthesis of the Rh(III), Ir(III), and Pt(II) octabutoxynaphthalocyanines

Table 1

¹H-NMR chemical shift of metal-free and metallo-Nc(OBu)₈

H	Rh	Ir	Ni	Pd	Pt
—	Cl-py	Cl-py	—	—	—
Nc					
1,4	8.94 m 8	8.91 m 8	8.90 m 8	8.95 m 8	8.93 m 8
2,3	7.86 m 8	7.84 m 8	7.84 m 8	7.87 m 8	7.87 m 8
OC ₄ H ₉					
C1	5.13 t 16	5.23 t 16	5.01 t 16	5.19 t 16	5.18 t 16
C2	2.21 m 16	2.23 m 16	2.18 m 16	2.24 m 16	2.24 m 16
C3	1.64 m 16	1.69 m 16	1.63 m 16	1.66 m 16	1.66 m 16
C4	1.01 t 24	1.06 t 24	1.01 t 24	1.03 t 24	1.03 t 24
py					
2,6	3.19 d 2	3.17 d 2			
3,5	5.72 t 2	5.68 t 2			
4	6.51 t 1	6.50 t 1			

Table 2
Photophysical Properties of $\text{MNC}(\text{OBU})_8$ ($\text{M} = \text{Zn(II)}, \text{Ni(II)}, \text{Pd(II)}, \text{Pt(II)}, \text{Co(II)}, \text{Rh(II)}, \text{Ir(III)}$) in benzene.^a

Metal	Z	λ_Q/nm	$10 \epsilon_Q/\text{M}^{-1}\text{cm}^{-1}$	λ_f/nm	Stokes shift/ cm^{-1}	q_M	λ_{ph}/nm
Zn	30	847	1.80	857	138	0.07	–
Ni	28	844	2.25	–	–	–	–
Pd	46	827	2.67	873	652	0.0061	1343
Pt	78	811	2.64	879	954	0.0017	1265
Co	27	832	1.68	–	–	–	1092 ^b
Rh	45	819	1.42	863	623	0.0023	1298
Ir	77	802	2.84	882	1131	0.0008	1235

^a pyridine (1%, by volume) was added to the solution of Zn and Rh complexes;

^b observed as a weak emission band upon 830 nm excitation, presumably from the $^2T_1(\pi, \pi^*)$ state [4b].