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Ligand-to-Metal Charge Transfer Excited States with Unprecedented Luminescence Yield in Fluid Solution

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A bridged d^0 zirconocene dichloride is reported as a first group 4 metal complex possessing rare long-lived ligand-to-metal charge transfer (LMCT) excited states with high emission yields and excited-state lifetimes in fluid solutions (e.g., $\Phi_{LUM} = 0.41$ and $\tau = 17.6\ \mu s$ in 1,2-dichlorobenzene at 20 °C). The basic emission parameters Φ_{LUM} and τ are shown to be extremely solvent-dependent in fluids at room temperature. The first principle dependences of LMCT emission parameters on solvent properties are revealed with use of the target complex. For fluid solutions, the linear correlation between Φ_{LUM} and τ is reported, thus suggesting that a solvent determines the rate constant for nonradiative decay, k_{nr}.

1. Introduction

Molecular electronic excited states are of great fundamental and technological importance. In coordination photophysics and photochemistry, research has traditionally concentrated on the search for long-lived excited states and utilization of their transformations in light energy conversion, information processing, and photocatalysis.[1−6] In spite of the substantial attention, devoted to design of molecules possessing long-lived, highly emissive excited states in fluids, there remains a great deal of uncertainty regarding the best choice of structural and electronic variations and how they can be best employed in predicting photophysical properties, such as luminescence efficiency. Accurate computational predictions of optical and other electronic properties for excited states have proved more difficult to obtain than for ground states.

There are very few examples of molecules possessing long-lived LMCT excited states, especially those emissive in fluid solution.[7] Much remains to be learned about LMCT excited states and medium effects. Although transition metal complexes have provided useful probes for studying solvent effects,[8] systematic research has never been addressed to the interaction between solvents of differing polarity and donating ability and complex molecules, having low-lying ^{3}LMCT states.

Transition metal complexes are an important class of materials in many areas of science and technology. Group 4 metal π-complexes have been found to promote various important catalytic and stochiometric transformations, however, the rational control of chemical and catalytic behavior and basic structure−property relationship remains a major challenge.[9] Recently, with the use of group 4 bent metallocenes, we developed the experimental approach for obtaining and correlating electrochemical and optical parameters to gain measurable information on HOMO, LUMO, and the HOMO−LUMO gap.[10] The origin of the lowest weak transition LMCT in the d^0 organometallics was justified to be a HOMO → LUMO transition (e.g., for metallocene dichlorides $(\pi\text{-L})_2MCl_2$: $[(\pi\text{-L})_2{}^{2-}M^{4+}Cl_2{}^{2-}] \rightarrow [(\pi\text{-L})_2{}^{-}M^{3+}Cl_2{}^{2-}]^*$). To elucidate further, we initiated a systematic study of LMCT excited states based on d^0 complexes Cp_2MCl_2 ($Cp = \eta^5\text{-}C_5H_5$, cyclopentadienyl) along group 4 transition metals.[11] Importantly, this pure L → M charge transfer between the frontier MOs originates the highly emissive (for the representative compounds Cp_2MCl_2 where M = Zr, Hf: $\Phi_{LUM} = 1$ at 77 K), long-lived (τ in the range of milliseconds at 77 K) state in group 4 metallocenes. This is also a rare case where phosphorescence from a coordination molecule, especially organometallic one, originates from pure LMCT states.[1,2,4,7,10,11] The present communication describes a bridged zirconocene(IV) dichloride *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ (**CBIZr**), where "rac" stands for the racemic isomer, C_6H_{10} is *trans*-cyclohexenylene bridge, and $IndH_4$ is η^5-(4,5,6,7-tetrahydro-1-indenyl) (see Chart 1), that exhibits markedly efficient, long-lived emission at room temperature (RT) in various media typically employed in catalysis, synthesis, etc. Along with this, we wish to report first principle dependences of room-temperature LMCT emission quantities of a complex, bearing a d^0 metal ion, on solvent properties as a part of our ongoing study.

2. Experimental Methods

The zirconocenes, as other group 4 parents, are air and moisture sensitive. The solvents (spectrophotometric grade, where possible) were additionally purified, rigorously dried by reflux over $LiAlH_4$ or CaH_2 and P_4O_{10} followed by distillation, and degassed through several freeze−pump−thaw cycles. All measurements and manipulations were carried out under strictly

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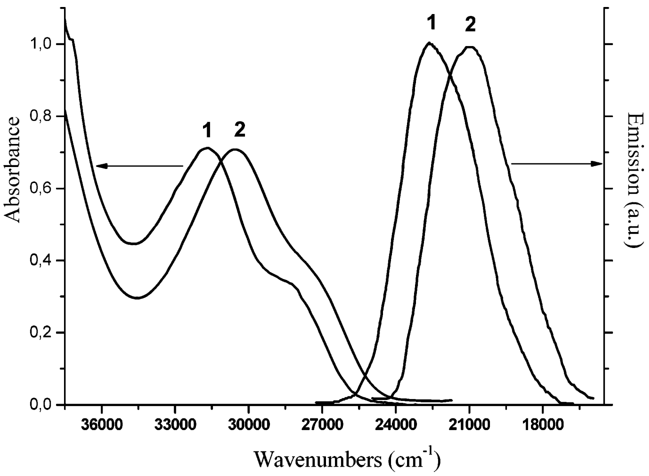
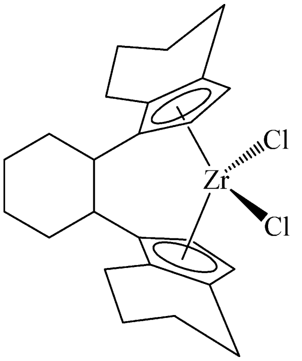


Figure 1. Absorption and emission spectral data for **CBIZr** dissolved in methylcyclohexane (1) and dichloromethane (2) at 20 °C. The emission spectra are normalized.

CHART 1: Molecular Structure of Racemic *trans*-1,2-[Bis(η^5-4,5,6,7-tetrahydro-1-indenyl)cyclohexane]zirconium(IV) Dichloride



anaerobic and anhydrous conditions under a high-purity inert (Ar or He) atmosphere in flame-dried glassware on a double-manifold high-vacuum line using standard Schlenk technique or on all-glass vacuum line fitted with high-vacuum Teflon stopcocks. Preparative and crystallographic data for **CBIZr** are given in the Supporting Information and will be discussed in depth in a forthcoming paper.

Absorption spectra were measured on a UV−vis−NIR scanning spectrophotometer UV-3101PC ("Shimadzu Corporation"). The conventional time-correlated single-photon counting technique was used for lifetime measurements by a Fluotime 200 spectrometer comprising a PDL800-B unit with external synchronization and a LDH-PC 375 laser diode head ("PicoQuant GmbH") as a source of exciting light ($\lambda_{ex} = 375$ nm) at RT. The details of photophysical experiments are provided by the Supporting Information.

TABLE 1: Room-Temperature Luminescence Parameters of CBIZr Dissolved in Nineteen Solvents at 20 °C (Measured for (0.9−1.3) × 10^{-4} M Solution, Otherwise Noted)

solvent	E_{00}/cm^{-1}	Φ_{LUM}	$\tau/\mu s^{d}$
dichloromethane	23800	0.32	14.07 ± 0.38
1,2-dichloroethane	23900	0.245	10.29 ± 0.29
carbon tetrachloride	24600	0.025	1.17 ± 0.03
bromotrichloromethane	24550	$0.0005 < \Phi < 0.005^{a,b}$	0.24 ± 0.01
benzene	24400	0.158^{c}	7.33 ± 0.13^{b}
toluene	24500	0.121	4.87 ± 0.08
ethylbenzene	24600	0.103	4.04 ± 0.07
sec-butylbenzene	24550	0.048	2.19 ± 0.03
o-xylene	24600	0.135	5.11 ± 0.29
m-xylene	24600	0.103	4.03 ± 0.06
p-xylene	24600	0.07	3.48 ± 0.06
1,2-dichlorobenzene	24200	0.41	17.60 ± 0.31
p-chlorotoluene	24150	0.137	5.70 ± 0.12
methyltetrahydrofuran	24500	0.009^{b}	0.68 ± 0.01
pentane	25100	0.015	0.79 ± 0.01
cyclohexane	25100	0.031	1.47 ± 0.02
methylcyclohexane	25100	0.027	1.31 ± 0.02
hexene-1	25000	0.008^{b}	0.52 ± 0.01
acetonitrile	23750	0.049	2.58 ± 0.05

[a] Determined upon excitation with a Hg high-vacuum lamp at 360 nm. [b] An approximate value, error may result from difficulties with solvent purification. [c] Measured for 2 × 10^{-4} M solution. [d] Measured upon excitation with a diode laser at 375 nm.

3. Results and Discussion

d^0 bent metallocene **CBIZr** is highly emissive (phosphorescent, see the Supporting Information) in organic glasses, in the solid state, and most interestingly, in fluid liquids at low and room temperature. Excitation into either the first or second LMCT transition [$\pi(\mathrm{IndH_4}^-) \rightarrow \mathrm{d(Zr)}$] results in the same long-lived emissive excited states; luminescence decay is single exponential. Representative absorption and luminescence spectra for the zirconocene are shown in Figure 1 (the HOMO-to-LUMO absorption appears as a shoulder in spectra, extinction coefficient of 1400 ± 100 mol^{-1} L cm^{-1}, being essentially the same in all media studied). In each case emission is broad, unstructured, and characteristic of a charge-transfer (CT) state, in general, and of LMCT states based on Cp_2ZrCl_2 reported earlier,[11] in particular. In contrast to **CBIZr**, neither parent Cp_2ZrCl_2 nor even more closely related *rac*-$C_2H_4(Ind)_2ZrCl_2$ are emissive in common solvents at RT. We attribute this effect to the enhance of steric hindrance and rigidity of the ligand framework via modification on the both bridging unit (the cyclic bridge *trans*-C_6H_{10}) and aromatic ligands (only two from five positions in C_5 rings left unsubstituted) also restricting rotation of the ligands, therefore, reducing the vibrational relaxation contribution.

Emission profiles are concentration and excitation wavelength independent throughout the region of the two lower-energy absorptions studied. Both two lower-energy LMCT absorption bands in the near-UV region shift to lower energy in increasingly polar solvents ($\lambda_{max1} = 350-364$ nm and $\lambda_{max2} = 315-328$ nm; e.g., see Figure 1) which is in line with a CT nature. Stokes shift ranges from ca. 5900 to 6900 cm^{-1} in different solvents. A larger Stokes shift is observed in the solvents with higher polarity, presumably due to a larger stabilization of the excited CT state in polar media.

An important aspect is that the emission quantum yield (Φ_{LUM}) and excited-state lifetime (τ) in fluid solutions appear to be highly sensitive to the external environment at RT (they span over 2 orders of magnitude; see Table 1), and those in various glassy media are essentially close at 77 K: $\Phi_{LUM} = 1$ and $\tau \approx 2$ ms, respectively. There are no systematic variations in Φ_{LUM} and τ with the trend in the bulk solvent parameters, such as dielectric constant ϵ, viscosity or a complex combination of the dielectric functions, e.g., $(\epsilon - 1)/(2\epsilon + 1) - (n_D^2 - 1)/(2n_D^2 + 1)$, and with the trend in dipole moments of solvent molecules. For this examined set of nineteen solvents, although the solvents being nonpolar or weakly polar (except for MeCN), the observations indicate that solvation response depends strongly upon the particular types of solvent−solute coupling present and the effects can be also caused by the specific ordering of solvent molecules in the solvent shells. The room-temperature quantum yield and lifetime approach their highest values of $\Phi_{LUM} = 0.41$ and $\tau = 1.76 \times 10^{-5}$ s, respectively, in 1,2-dichlorobenzene, surpassing those of major known metal-based luminophores[12] and, to the best of our knowledge, surpassing those of LMCT excited states reported in literature.

We suppose that *strong outer-sphere solvation restricts conformational freedom* and leads to more rigid, "frozen" architecture of the complex ("rigid matrix" effect at microscopic level), thus reducing vibrational relaxation of **CBIZr**, *and also depresses dynamic bimolecular quenching*. For **CBIZr**, energy gap law has no major influence on the emission yield and excited-state lifetime in different solvents (one would hardly expect dramatic changes in Φ_{LUM} and τ with small energy gap variations ΔE: $\Delta E_{00} = 0.17$ eV and $\Delta E_{max} = 0.23$ eV, i.e., 5−8% from the values of E_{00} or E_{max}); meanwhile, the suppressing of vibrational relaxation by a stronger solvent shell is thought to be a crucial factor. (Here the dramatic enhancements in Φ_{LUM} and τ were observed even upon minor reduction of the energy gap of **CBIZr** in different solvents at RT, e.g., in 1,2-dichlorobenzene, dichloromethane, 1,2-dichloroethane). For **CBIZr** and, most probably, for closely related complexes, not a value of energy gap ΔE, but a solvent (i.e., "rigidity of a solvent shell") determines the rate constant for nonradiative deactivation of excited states (k_{nr}), which is revealed by a drastic change in basic parameters Φ_{LUM}, τ.

Solvation depends on macroscopic medium properties (ϵ, n_D^2, etc.) and specific (coordinative, orbital) interaction with a solute (i.e., nonspecific and specific solvation components). Because van-der-Waals interactions are not the controlling factor here (perhaps, with exception for saturated hydrocarbons), we considered specific pair interactions (specific bonding effects) between the solute and a solvent where an important aspect is environmental steric requirements: e.g., aromatic solvents may bind at the periphery of the coordination sphere (aromatic ligand sites), forming charge-transfer complexes or the related structures involving π-donor and π-acceptor interactions, and also directly to the metal ion (although the metal is somehow embedded within the ligand sphere).

Accordingly, the emission quantities (Φ_{LUM} and τ) of bulky **CBIZr** appear to be dependent on small structural variations in the surrounding medium, such as degree of steric hindrance imposed by the substituent(s) in solvent molecules. In fact, the Φ_{LUM} and τ values are smaller for the related solvents with bulkier structures, e.g., for benzene derivatives. (Notably, these are typical specific solvating agents with respect to metallocenes possessing nearly identical quantities ϵ and n_D^2 and close solvatochromic effects with respect to **CBIZr**, e.g., close or equal shifts of E_{00} and E_{max}.) Intriguing findings are the linear correlations (Figures 2a and 3a). Precisely, we obtained the relation with alkyl substituent length (and also Taft substituent steric constant E_s^o) in homologous alkylbenzenes: a linear decrease of Φ_{LUM} (Figure 2a) and τ of **CBIZr** is observed with the increasing number of *C*-atoms in the alkyl substituent in the solvent molecules. (For these aromatics, we also observed the linear enhancement in Φ_{LUM} with a very small increase in n_D^2, Figure 2b). In the same vein, cooperative substituent effects have a significant impact on the solvent dependence of the basic characteristics Φ_{LUM} and τ: a linear decrease with increasing parameter θ. We used to suggest a new parameter (θ, the angle between the extensions of $C_{ring}{-}C_{Me}$ bonds) to characterize a steric factor, introduced by the solvent at microscopic level: reduced accessibility of the polarizable π-electron system of aromatic solvents for anisotropic coordinative (orbital) interaction with the aromatic π-system of two C_5 rings of **CBIZr** (Figure 3a). We conclude that in the case of *p*-xylene, the π-electron system of the C_6 ring of the solvent molecules is more sterically shielded from coordination with the solute (as compared to other isomers: *o*- and *m*-xylenes). Moreover, owing to higher steric hindrance of most distant methyl substituents in the C_6 ring, coordinative interaction (or close contact) of only one C═C fragment of the aromatic C_6 ring of *p*-xylene with the solute is most probable, in contrast to less hindered *o*- and *m*-xylenes (where two C═C bonds are accessible for coordination).

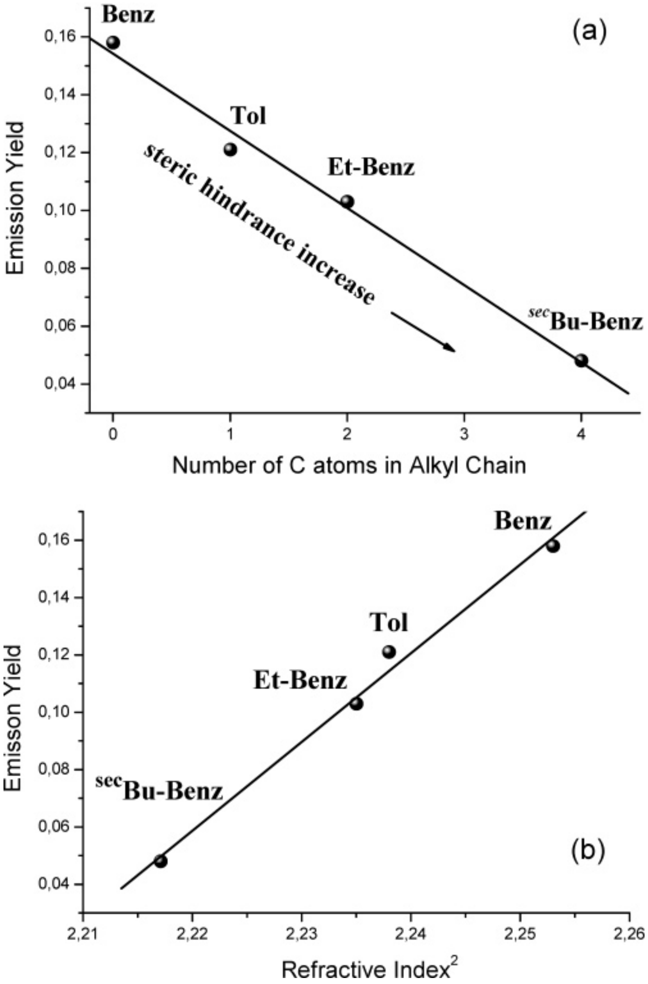


Figure 2. Linear dependences of room-temperature emission efficiency of **CBIZr** dissolved in nonsubstituted (Benz) and alkyl-substituted benzenes (Tol = toluene, Et-Benz = ethylbenzene, ^{sec}Bu-Benz = *sec*-butylbenzene) on the solvent quantities: (a) number of carbon atoms in the alkyl substituent in C_6-ring and (b) optic dielectric constant $(n_D^{20})^2$ (where n_D^{20} is the index of refraction).

Notably, the derived τ values vary over a wide range, spanning from 2.4×10^{-7} to 1.76×10^{-5} s within the studied solvent series. In some solvents, **CBIZr** is a sufficiently weak emitter; accordingly, the lifetime there is dominated by nonradiative deactivation: $\tau^{-1} \sim k_{nr}$. In marked contrast, within the precision of our measurements, the radiative rate constant, $k_r = 2.35 \times 10^4$ s^{-1}, remains virtually independent of the nature of the solvent. This follows from the excellent linear correlation between the experimental quantities Φ_{LUM} and τ (s), viz. $\Phi_{LUM} = -0.002 + 23480\tau \approx 2.35 \times 10^4\tau$, $r^2 = 0.998$ (Figure 4), the slope of the plot being the rate constant for radiative decay, k_r. In these limits, we estimate a maximal lifetime of 43 μs for a RT solution. To the best of our knowledge, a linear relation $\Phi_{LUM} \propto \tau$ is for the first time reported. The precision of the data and their at least 2 orders of magnitude difference are sufficient to show that the linear relation pattern is real. The

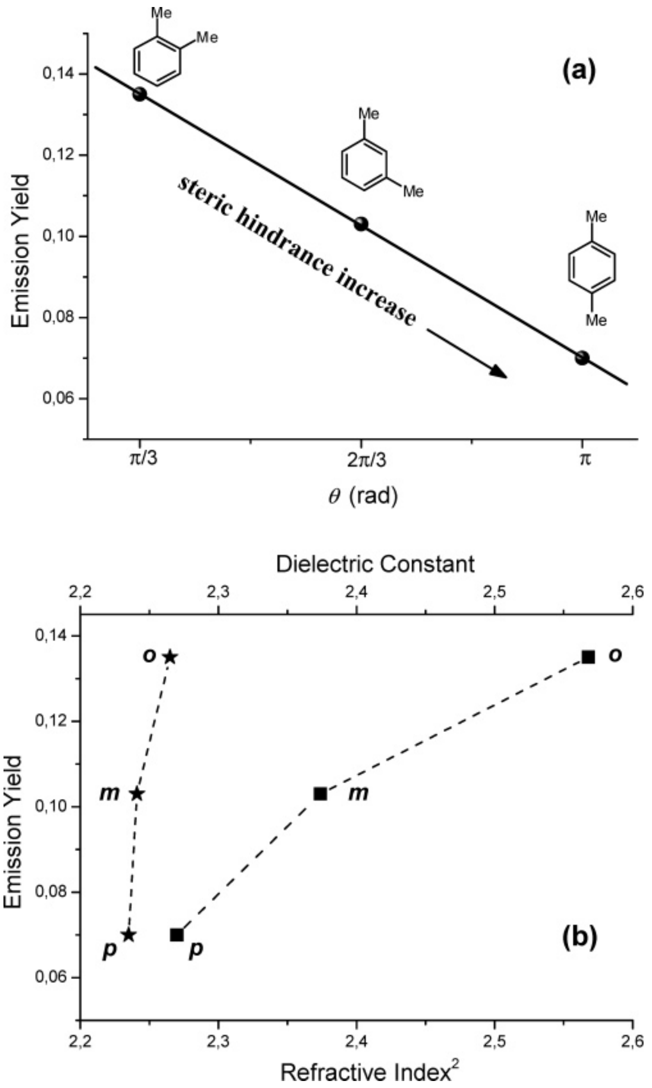


Figure 3. Dependences of room-temperature emission efficiency of **CBIZr** dissolved in (*o*, *m*, *p*)-xylenes on the angle between the extensions of C$_{ring}$−C$_{Me}$ bonds in the solvent molecule (a) and the solvent macroscopic parameters: ϵ (designated by squares) and $(n_D^{20})^2$ (designated by stars) (b). The dash lines in (b) are merely the guide to the eye.

principle correlation is rationalized by assuming that the nature of the states involved in photoexcitation and emission remains essentially the same for **CBIZr** dissolved in various media.

4. Conclusions

In summary, we have observed, for the first time, remarkable room-temperature LMCT emission (phosphorescence) from a mononuclear group 4 metal complex **CBIZr** in fluid solutions by choosing Zr(IV) as a d^0 central ion and the aromatic ligand substituents of sufficient steric bulk, inhibiting the rings rotation therefore yielding a rigid molecular framework. The RT emission efficiency and the excited-state lifetime of **CBIZr** dissolved in 1,2-dichlorobenzene are 0.41 and 17.6 μs, respectively, surpassing those of pure LMCT excited states in fluid media reported to date. The observed strong solvent-effect trends cannot be explained by electrostatic or/and general (van-der-Waals) interactions; however, they indicate significant specific (outer-sphere coordinative) interactions between the d^0 complex and a surrounding solvent. As a general conclusion, we suppose that a conformational locking effect induced by appropriately positioned substituents in a d^0 metallocene and strong outer-sphere solvent shell(s) should restrict structural relaxation within excited states, enhance the emission yield, and also extend the lifetime.

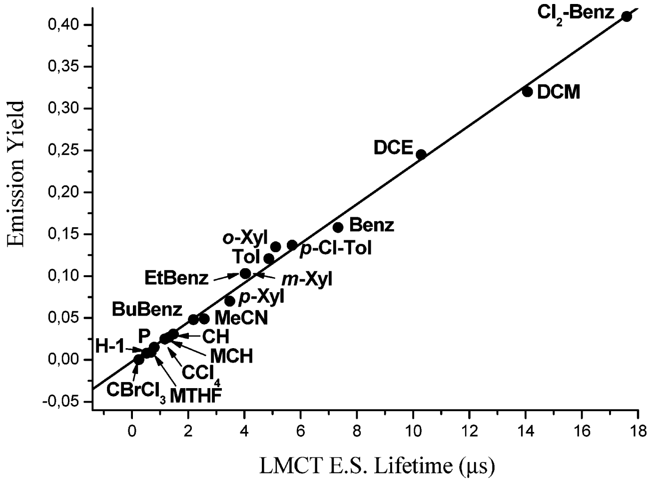


Figure 4. Linear correlation between the independent experimental values of the luminescence quantum yield and ^{3}LMCT lifetime obtained at RT for **CBIZr** dissolved in the nineteen aprotic solvents. Solvents: Cl$_2$-Benz = 1,2-dichlorobenzene, DCM = dichloromethane, DCE = 1,2-dichloroethane, Benz = benzene, *p*-Cl-Tol = *p*-chlorotoluene, (*o*, *m*, *p*)-Xyl = (*o*, *m*, *p*)-xylene, Tol = toluene, EtBenz = ethylbenzene, ^{sec}Bu-Benz = *sec*-butylbenzene, CH = cyclohexane, MCH = methylcyclohexane, P = pentane, H-1 = hexene-1, MTHF = 2-methyltetrahydrofuran. The linear plot represents the least-squares best fit to the data points with a slope of 23 480 s^{-1}.

Another consequence of the study is that it establishes a linear relation $\Phi_{LUM} \propto \tau$ for ^{3}LMCT excited states, giving the constant value of k_r (ca. 2×10^4 s^{-1} at 20 °C), characteristic of **CBIZr** and indifferent to the variations in identity of the external medium. Thus, the chromophoric basis for the excited states remains the same throughout the series regardless of how the solvent−solute interactions vary at the microscopic level. A full accounting of the solvent effects on emission properties of d^0 complexes requires a further complex study.

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Supporting Information Available: Synthesis, crystallographic data for **CBIZr**, and photophysical experiments, including a table of cell parameters, molecular structures, a synthetic scheme, an excited-state diagram, and an emission spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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