

Chromophore-Functionalized Phenanthro-diimine Ligands and Their Re(I) Complexes

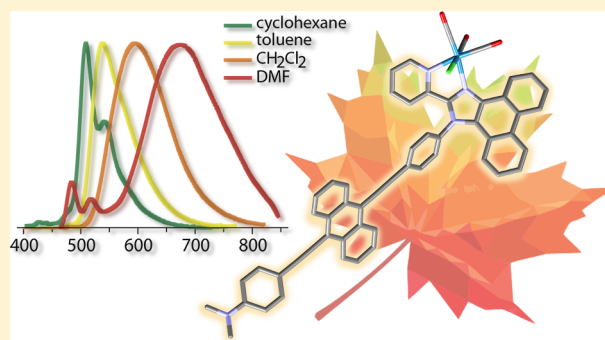
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Supporting Information

ABSTRACT: A series of diimine ligands has been designed on the basis of 2-pyridyl-1*H*-phenanthro[9,10-*d*]imidazole (**L1**, **L2**). Coupling the basic motif of **L1** with anthracene-containing fragments affords the bichromophore compounds **L3–L5**, of which **L4** and **L5** adopt a donor–acceptor architecture. The latter allows intramolecular charge transfer with intense absorption bands in the visible spectrum (lowest λ_{abs} 464 nm ($\epsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 490 nm ($\epsilon = 5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in CH_2Cl_2 for **L4** and **L5**, respectively). **L1–L5** show strong fluorescence in a fluid medium ($\Phi_{\text{em}} = 22–92\%$, λ_{em} 370–602 nm in CH_2Cl_2); discernible emission solvatochromism is observed for **L4** and **L5**. In addition, the presence of pyridyl (**L1–L5**) and dimethylaminophenyl (**L5**) groups enables reversible alteration of their optical properties by means of protonation. Ligands **L1–L5** were used to synthesize the corresponding $[\text{Re}(\text{CO})_3\text{X}(\text{diimine})]$ ($\text{X} = \text{Cl}$, **1–5**; $\text{X} = \text{CN}$, **1-CN**) complexes. **1** and **2** exhibit unusual dual emission of singlet and triplet parentage, which originate from independently populated $^1\pi\pi^*$ and $^3\text{MLCT}$ excited states. In contrast to the majority of the reported Re(I) carbonyl luminophores, complexes **3–5** display moderately intense ligand-based fluorescence from an anthracene-containing secondary chromophore and complete quenching of emission from the $^3\text{MLCT}$ state presumably due to the triplet–triplet energy transfer ($^3\text{MLCT} \rightarrow ^3\text{ILCT}$).



INTRODUCTION

Multichromophore compounds, i.e. species combining two or more photofunctional units, offer wide possibilities to manipulate the energy of electronic transitions on the molecular level and consequently within the bulk materials. Depending on the properties of the constituting blocks and the interplay between them, such molecules can be utilized for a diversity of light-harvesting, light-emitting, and charge transport purposes.^{1–4} The efficiency of the targeted photophysical processes is defined by the dynamics of the excited state, which can be chemically tuned by proper molecular design.

An appealing approach to systems demonstrating unconventional photophysical behavior involves coupling of an organic chromophore with a transition-metal ion.⁵ The presence of a d-block ion participating in the electronic transitions (e.g., metal to ligand or ligand to metal charge transfer, MLCT/LMCT) increases the number of accessible excited states. Furthermore, spin–orbit coupling induced by the heavy atom often activates fast intersystem crossing (ISC), leading to lower energy emissive states with triplet spin multiplicity.⁶ Minimization of the electronic interaction between organic and metal-containing fragments in these molecules, e.g. by providing large spatial separation and/or by the lack of direct conjugation, may decouple the fluorescent and phosphorescent emitters to give

dual singlet–triplet emission, suitable for ratiometric sensing^{7–10} and panchromatic light generation.¹¹ In some cases even direct attachment of the metal center to the extended organic chromophore affords dual-emissive compounds^{12–15} or complexes demonstrating prompt fluorescence¹⁶ because of slow ISC rates. Nevertheless, the majority of the bi- or multichromophore metal–organic assemblies undergo efficient intramolecular energy transfer,^{5,17–19} which makes these compounds fundamentally important for luminescent sensing,^{20,21} singlet oxygen generation (photodynamic therapy),^{22–24} and triplet–triplet annihilation upconversion.^{25,26}

From a preparative viewpoint, one facile way to construct the metal–organic architectures relies on the coordination of the metal center to a presynthesized chromophore ligand. In this respect the rhenium(I) carbonyl diimine derivatives constitute an attractive and readily accessible class of photoactive complexes. These compounds play a noticeable role in bioimaging and photocatalysis^{27–30} due to robust stereochemistry of the $\{\text{Re}(\text{CO})_x(\text{diimine})\}$ ($x = 2, 3$) motif and its tailorability and rich photophysical behavior, dominated by

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the diimine-defined (MLCT or ligand-centered, LC) triplet excited state.³¹

Representative diimines containing extended aromatic systems or functionalized with an ancillary fluorophore, which are shown in Figure 1, have been successfully employed for the

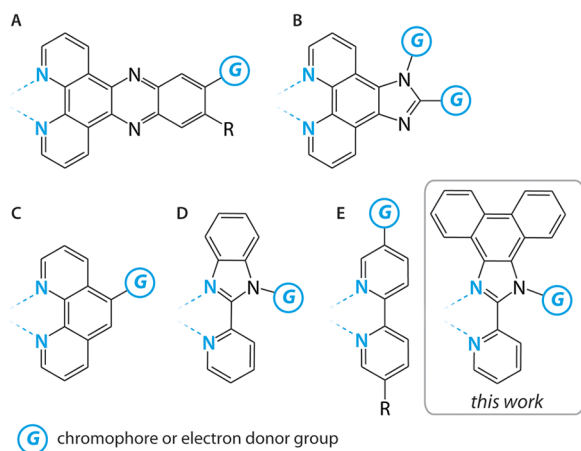


Figure 1. Representative chromophore diimine ligands used for the synthesis of rhenium(I) carbonyl complexes.

preparation of rhenium(I) carbonyl species. Extensive research efforts have been devoted to the compounds built on the family of dipyridophenazine ligands (A), the majority of which undergo formation of the dark (nonemissive) phenazine-localized triplet excited states of either ligand-centered (³LC) or intraligand charge transfer (³ILCT) nature.^{32–36} On the other hand, Re(I) complexes based on phenanthroline-imidazole ligands (B) bearing electron donor (triphenylamine) groups display moderately intense MLCT/ILCT phosphorescence,³⁷ while for those with naphthalene and coumarin fragments luminescence is largely quenched due to the population of the low-lying ³LC(chromophore) states from the ³MLCT states.³⁸ A similar triplet–triplet energy transfer, which occurs in a “ping-pong” manner, has been found for phenanthroline (C)³⁹ and pyridyl-benzimidazole (D)⁴⁰ ligands decorated with *N*-(1,10-phenanthroline)-4-(1-piperidinyl)naphthalene-1,8-dicarboximide and anthracene chromophores. In the case of phenanthrolines (C), bipyridines (E), and related ligands, anchoring the extended electron-rich groups results in intraligand charge transfer and a dominating triplet emission of ILCT and MLCT parentage.^{41–45}

Recently, pyridyl-imidazoles fused with pyrene and phenanthrene motifs have been shown to serve as efficient chelating functions in Ru(II), Os(II), and Ir(III) complexes despite the steric hindrance introduced by the polyaromatic cores.^{46,47} Inspired by this preparative success and rich photophysical behavior of Re(I) diimine carbonyl compounds, herein the coordinating pyridyl-phenanthroimidazole motif (Figure 1) has been employed for the construction of donor–acceptor bichromophore dyes. We have synthesized the derivatives of 1-phenyl- and 1-(4-bromophenyl)-2-(pyridin-2-yl)-1*H*-phenanthro[9,10-*d*]imidazole ligands (L1 and L2) tailored to ethynyl-connected chromophores (anthracene, L3; diphenylamino-anthracene, L4; anthracene-ethynyl-dimethylaniline, L5), which were further used to generate the series of rhenium(I) chloro tricarbonyl complexes [Re(CO)₃X(diimine)] (X = Cl, 1–5; X = CN, 1-CN).

EXPERIMENTAL SECTION

General Comments. The solution ¹H and ¹H–¹H COSY NMR spectra were recorded on Bruker Avance 400 and AMX 400 spectrometers with chemical shifts referenced to residual solvent resonances. The infrared spectra were measured on a Shimadzu FTIR-8400S instrument. Mass spectra were recorded on a Bruker maXis II ESI-QTOF instrument in the ESI⁺ and ESI[−] (for 2–5) modes. Microanalyses were performed in the analytical laboratory of the University of Eastern Finland. The synthesis of the ligands (L1–L5) are provided in the Supporting Information.

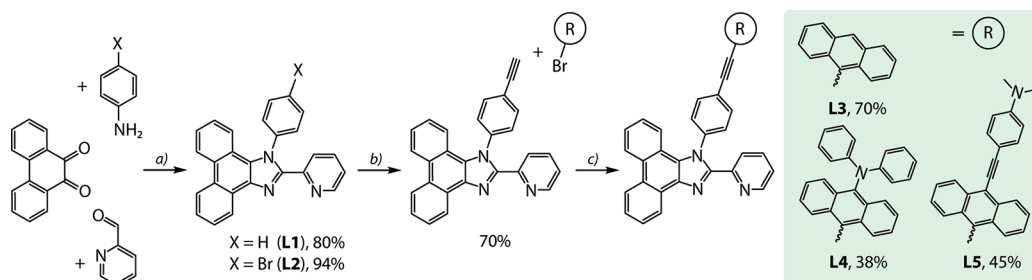
Synthesis of Complexes Re(CO)₃Cl(L1–L5) (1–5). Pentacarbonylrhenium(I) chloride (100 mg, 0.28 mmol) and a stoichiometric amount of the corresponding ligand L1–L5 (0.29 mmol) were suspended in ethanol (30 mL) and degassed by purging nitrogen for 15 min with stirring. The reaction mixture was refluxed for 5 h under a nitrogen atmosphere to give a yellow (1–3), orange (4), or red (5) suspension. The precipitate was collected, washed with ethanol and diethyl ether, dried, and purified by recrystallization.

Re(CO)₃Cl(L1) (1). Recrystallized by slow evaporation of its toluene solution to give bright yellow crystalline material (180 mg, 96%). IR (CH₂Cl₂, $\nu(\text{CO})$ cm^{−1}): 2024s, 1921s, 1894s. ¹H NMR (DMSO-*d*₆, 298 K; δ): 9.34 (d, *J*_{HH} = 7.9 Hz, 1H), 9.21 (d, *J*_{HH} = 5.4 Hz, 1H), 9.01 (m, 2H), 8.14–7.83 (m, 7H), 7.72–7.61 (m, 3H), 7.42 (t, *J*_{HH} = 7.9 Hz, 1H), 7.02 (d, *J*_{HH} = 8.4 Hz, 1H), 6.80 (d, *J*_{HH} = 8.4 Hz, 1H). ESI⁺ MS (*m/z*): 698.04 [M + Na]⁺ (calcd 698.04). Anal. Calcd for C₂₉H₁₇ClN₃O₃Re: C, 51.44; H, 2.53; N, 6.21. Found: C, 51.51; H, 2.58; N, 6.25.

Re(CO)₃CN(L1) (1-CN). Complex 1 (100 mg, 0.15 mmol) and silver cyanide (22 mg, 0.16 mmol) were suspended in acetonitrile (60 mL), and the mixture was refluxed for 3 h under a nitrogen atmosphere in the absence of light. The suspension was cooled to room temperature and filtered through Celite, and the solvent was removed under reduced pressure. The solid residue was recrystallized by a gas-phase diffusion of diethyl ether into a dichloromethane solution of 1-CN at room temperature to give a bright yellow crystalline material (90 mg, 90%). IR (CH₂Cl₂, $\nu(\text{CO})$ cm^{−1}): 2024s, 1926s, 1914s. ¹H NMR (DMSO-*d*₆, 298 K; δ): 9.33 (dd, *J*_{HH} = 8.1 and 1.2 Hz, 1H), 9.23 (d, *J*_{HH} = 5.2 Hz, 1H), 9.03 (dd, *J*_{HH} = 8.1 and 5.2, 2H), 8.15 (m, 1H), 8.08 (dt, *J*_{HH} = 8.1 and 1.2 Hz, 1H), 8.02–7.92 (m, 4H), 7.88 (dd, *J*_{HH} = 7.7 and 1.2 Hz, 1H), 7.75–7.69 (m, 3H), 7.45 (dd, *J*_{HH} = 7.7 and 0.8 Hz, 1H), 7.04 (d, *J*_{HH} = 7.7 Hz, 1H), 6.83 (d, *J*_{HH} = 8.1 Hz, 1H). ESI⁺ MS (*m/z*): 689.07 [M + Na]⁺ (calcd 689.07). Anal. Calcd for C₃₀H₁₇N₄O₃Re: C, 53.97; H, 2.57; N, 8.39. Found: C, 53.79; H, 2.65; N, 8.31.

Re(CO)₃Cl(L2) (2). Recrystallized by a gas-phase diffusion of diethyl ether into a dichloromethane solution of 2 at room temperature to give a bright yellow crystalline material (200 mg, 95%). IR (CH₂Cl₂, $\nu(\text{CO})$ cm^{−1}): 2025s, 1922s, 1895s. ¹H NMR (DMSO-*d*₆, 298 K; δ): 9.33 (d, *J*_{HH} = 8.3 Hz, 1H), 9.21 (d, *J*_{HH} = 5.5 Hz, 1H), 9.02 (m, 2H), 8.22–8.10 (m, 4H), 7.96 (t, *J*_{HH} = 7.8 Hz, 1H), 7.86 (t, *J*_{HH} = 7.8 Hz, 1H), 7.75–7.67 (m, 2H), 7.58 (dd, *J*_{HH} = 8.3 and 2.5 Hz, 1H), 7.51 (t, *J*_{HH} = 7.8 Hz, 1H), 7.06 (d, *J*_{HH} = 8.3 Hz, 1H), 6.91 (d, *J*_{HH} = 8.3 Hz, 1H). ESI[−] MS (*m/z*): 787.93 [M + Cl][−] (calcd 787.93), 797.96 [M + HCOO][−] (calcd 797.96). Anal. Calcd for C₂₉H₁₆BrClN₃O₃Re: C, 46.07; H, 2.13; N, 5.56. Found: C, 46.08; H, 2.15; N, 5.62.

Re(CO)₃Cl(L3) (3). Recrystallized by a gas-phase diffusion of diethyl ether into acetone/methanol solution of 3 at room temperature to give bright yellow crystalline material (236 mg, 96%). IR (CH₂Cl₂, $\nu(\text{CO})$ cm^{−1}): 2025s, 1922s, 1894s. ¹H NMR (DMSO-*d*₆, 298 K; δ): 9.36 (d, *J*_{HH} = 8.1 Hz, 1H), 9.24 (d, *J*_{HH} = 5.3 Hz, 1H), 9.04 (m, 2H), 8.81 (s, 1H), 8.75 (d, *J*_{HH} = 8.1 Hz, 2H), 8.49 (dd, *J*_{HH} = 8.1 and 1.8 Hz, 1H), 8.40 (dd, *J*_{HH} = 8.1 and 1.8 Hz, 1H), 8.30 (dd, *J*_{HH} = 8.1 and 1.8 Hz, 1H), 8.24 (d, *J*_{HH} = 8.4 Hz, 2H), 8.16 (t, *J*_{HH} = 8.1 Hz, 1H), 7.98 (t, *J*_{HH} = 7.8 Hz, 1H), 7.88 (t, *J*_{HH} = 7.8 Hz, 1H), 7.80–7.65 (m, 7H), 7.54 (t, *J*_{HH} = 7.8 Hz, 1H), 7.21 (d, *J*_{HH} = 8.1 Hz, 1H), 7.04 (d, *J*_{HH} = 8.1 Hz, 1H). ESI[−] MS (*m/z*): 910.08 [M + Cl][−] (calcd 910.08), 920.11 [M + HCOO][−] (calcd 920.11). Anal. Calcd for C₄₅H₂₅ClN₃O₃Re: C, 61.60; H, 2.87; N, 4.79. Found: C, 61.80; H, 3.13; N, 4.87.

Scheme 1. Synthesis of Ligands L1–L5^a

^aReagents and conditions: (a) NH₄OAc, toluene/AcOH, 68 °C, N₂, 12 h; (b) X = Br, HC₂SiMe₃, *n*-propylamine, Pd(PPh₃)₄, CuI, 57 °C, N₂, 48 h, then K₂CO₃ in THF/MeOH for 1 h; (c) *n*-propylamine, Pd(PPh₃)₄, CuI, 57 °C, N₂, 48 h.

Re(CO)₃Cl(L4) (4). Recrystallized by slow evaporation of its ethanol/dichloromethane solution at room temperature to give a bright orange crystalline material (280 mg, 96%). IR (CH₂Cl₂, ν (CO) cm⁻¹): 2025s, 1922s, 1894s. ¹H NMR (DMSO-*d*₆, 298 K; δ): 9.37 (d, *J*_{HH} = 7.8 Hz, 1H), 9.24 (d, *J*_{HH} = 4.6 Hz, 1H), 9.04 (m, 2H), 8.86 (d, *J*_{HH} = 8.4 Hz, 2H), 8.52 (d, *J*_{HH} = 8.2 Hz, 1H), 8.42 (d, *J*_{HH} = 8.2 Hz, 1H), 8.31 (d, *J*_{HH} = 8.2 Hz, 1H), 8.19–8.13 (m, 3H), 7.98 (t, *J*_{HH} = 7.8 Hz, 1H), 7.88 (t, *J*_{HH} = 7.8 Hz, 1H), 7.82–7.70 (m, 6H), 7.62 (m, 2H), 7.55 (t, *J*_{HH} = 7.8 Hz, 1H), 7.26–7.21 (m, 5H), 7.06–6.99 (m, 4H), 6.94 (t, *J*_{HH} = 7.4 Hz, 2H). ESI⁻ MS (*m/z*): 1077.15 [M + Cl]⁻ (calcd 1077.15), 1087.18 [M + HCOO]⁻ (calcd 1087.18). Anal. Calcd for C₅₇H₃₄ClN₄O₃Re: C, 65.54; H, 3.28; N, 5.36. Found: C, 65.22; H, 3.39; N, 5.31.

Re(CO)₃Cl(L5) (5). Recrystallized by a gas-phase diffusion of diethyl ether into a dichloromethane/ethanol solution of 5 at room temperature to give a bright red crystalline material (274 mg, 96%). IR (CH₂Cl₂, ν (CO) cm⁻¹): 2025s, 1922s, 1894s. ¹H NMR (DMSO-*d*₆, 298 K; δ): 9.37 (d, *J*_{HH} = 8.1 Hz, 1H), 9.24 (d, *J*_{HH} = 5.3 Hz, 1H), 9.04 (m, 2H), 8.81 (m, 2H), 8.72 (m, 2H), 8.51 (m, 1H), 8.41 (m, 1H), 8.30 (m, 1H), 8.16 (m, 1H), 7.98 (t, *J*_{HH} = 7.8 Hz, 1H), 7.90–7.69 (m, 10H), 7.54 (t, *J*_{HH} = 7.8 Hz, 1H), 7.22 (d, *J*_{HH} = 8.4 Hz, 1H), 7.04 (d, *J*_{HH} = 8.4 Hz, 1H), 6.84 (d, *J*_{HH} = 8.8 Hz, 2H), 3.03 (s, 6H). ESI⁻ MS (*m/z*): 1053.15 [M + Cl]⁻ (calcd 1053.15), 1063.18 [M + HCOO]⁻ (calcd 1063.18). Anal. Calcd for C₅₅H₃₄ClN₄O₃Re: C, 64.73; H, 3.36; N, 5.49. Found: C, 64.4; H, 3.48; N, 5.61.

X-ray Structure Determinations. The crystals of L1, L5, 1, 1-CN, 2, and 5 were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 150 or 100 K (L5). The structures were determined on Bruker Kappa Apex II and Agilent Technologies Xcalibur diffractometers using Mo K α (λ = 0.71073 Å) and Cu K α (λ = 1.54184 Å) radiation, respectively. The APEX2⁴⁸ and CrysAlisPro⁴⁹ program packages were used for cell refinements and data reductions. A semiempirical or numerical absorption correction (SADABS⁵⁰ or SCALE3 ABSPACK⁴⁹) was applied to all data. The structures were solved by direct methods using the SHELXS-2014⁵¹ program with the WinGX⁵² graphical user interface. Structural refinements were carried out using SHELXL-2014.⁵¹ The crystallization solvent molecules in 1-CN could not be resolved unambiguously; their contribution to the calculated structure factors was taken into account by using a SQUEEZE⁵³ routine of PLATON.⁵⁴ The missing solvent was not taken into account in the unit cell content.

All non-H atoms were anisotropically refined, and all hydrogen atoms were positioned geometrically and constrained to ride on their respective parent atoms with C–H = 0.89–0.99 Å and *U*_{iso} = 1.2–1.5*U*_{eq}(parent atom). The crystallographic details are summarized in Table S1.

Photophysical Measurements. Freshly distilled solvents (cyclohexane, toluene, dioxane, chlorobenzene, *o*-dichlorobenzene, dichloromethane, dimethylformamide, and acetonitrile) were used for the solution experiments. For complexes 1–5, all solutions were carefully degassed before lifetime and quantum yield measurements by three “freeze–pump–thaw” cycles. UV–vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. The excitation and emission spectra in solution were measured on a HORIBA

FluoroMax-4 spectrofluorometer. Lifetimes were monitored on a HORIBA Scientific FluoroLog-3 spectrofluorometer. The emission quantum yields were determined by the comparative method⁵⁵ using coumarin 102 in ethanol (Φ_r = 0.764) as a standard with the refractive indexes of dichloromethane and ethanol equal to 1.42 and 1.36, respectively. The uncertainties of the quantum yield determinations were in the range of \pm 5% (an average of three measurements).

Computational Details. Electronic structure calculations were performed with the Gaussian 16 program package⁵⁶ within the framework of DFT/TD-DFT using the PBE0^{57,58} hybrid density functional. A 6-311G+(d) basis set was used for the calculations involving pure ligands, while a def2-TZVPPD/6-311G(d) (Re/other atoms) basis set was used for the rhenium complexes.⁵⁹ The natures of the stationary points were confirmed by calculating the vibrational frequencies for the optimized S₀, S₁, and T₁ geometries. Calculations were performed in dichloromethane solvent using the C-PCM method.^{60,61} Ground state S₀ optimizations were also performed under vacuum for comparison between X-ray structures.

RESULTS AND DISCUSSION

Synthesis and Characterization. The family of chelating ligands based on a 2-pyridyl-1*H*-phenanthro[9,10-*d*]imidazole core was prepared according to the reaction sequence summarized in Scheme 1. The 1-phenyl (L1)⁴⁷ and 1-(4-bromophenyl) (L2) derivatives were synthesized in good yields (80% and 94%, respectively) by the Debus–Radziszewski method starting from phenanthrene-9,10-dione, 2-pyridinecarboxaldehyde, and the corresponding aniline (see the Supporting Information for the experimental details). The subsequent two-step Sonogashira cross-coupling allows for the conversion of Br-aryl intermediate L2 into the anthracene-functionalized compounds, which were isolated in moderate yields (38–70%) as yellow (L3, L4) and red (L5) crystalline solids, soluble in common organic solvents.

The ESI⁺-MS of L1–L5 display the dominating signals corresponding to the protonated molecular ions at *m/z* 372.15, 450.05, 572.21, 739.28, and 715.28, respectively (Figure S1, Supporting Information). The ¹H NMR spectra of these compounds display well-resolved multiplets in the aromatic region (Figure S2), which were assigned on the basis of 2D ¹H–¹H COSY experiments; their multiplicities and relative intensities are completely compatible with the structural patterns shown in Scheme 1.

The structures of L1 and L5 were established by XRD analysis (Figure 2 and Figure S3). Their molecular arrangements found in the solid state are in agreement with the spectroscopic data obtained in solution. The phenanthroimidazole core in both ligands is nearly flat, as well as the anthracenyl motif in L5.

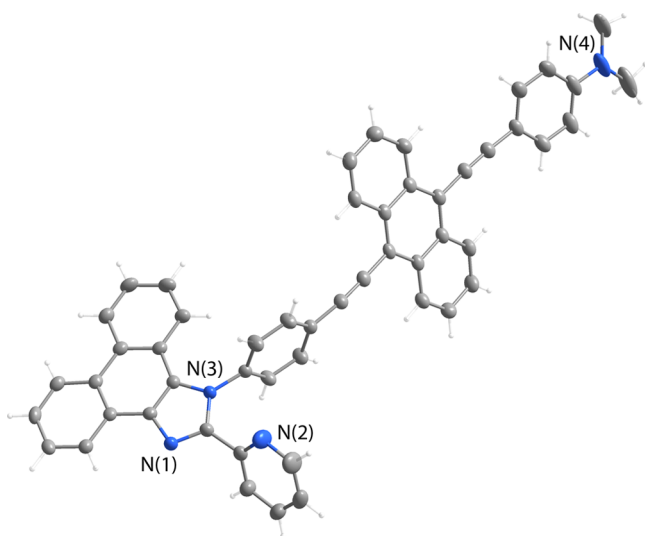


Figure 2. Molecular view of ligand **L5** (thermal ellipsoids are shown at the 50% probability level).

The planes of N(3)-bound phenyl(ene) rings in **L1** and **L5** are almost perpendicular to those of the imidazole fragment (the angles are 80 and 90° for **L1** for two independent molecules and 85° for **L5**), indicating that the conjugation between the polyaromatic moieties in chromophore-functionalized ligands **L3–L5** is most probably disrupted.

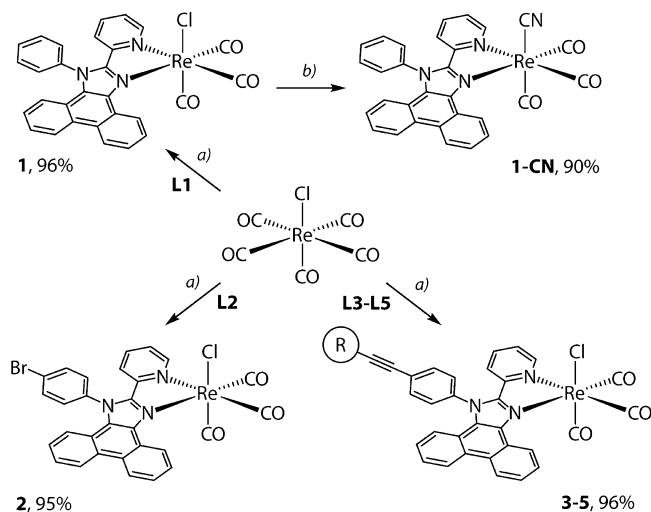
Despite the fact that the NMR data suggest unrestricted rotation of the C₆H₄ ring around the N(3)–carbon bond in solution at room temperature, it is reasonable to propose that the preferable conformation in the fluid medium corresponds to that found in the crystal due to the minimized intramolecular H–H repulsion. This conclusion is also supported by the computational analysis of the optimized geometries (Supporting Information). The crystal packing of **L5** reveals extensive intermolecular interactions (Figure S4), which evidently cause visible bending of the extended –C₆H₄–C₂–An–C₂–C₆H₄–fragment.

The coordinating ability of the pyridyl-imidazole chelating moiety, fused with sterically demanding polyaromatic systems (phenanthrene, pyrene), has been successfully demonstrated for some late-transition-metal ions (Ir(III), Os(II), Ru(II)).^{46,47,62} Similarly, ligands **L1–L5** can be employed for binding the {Re(CO)₃Cl} fragment to give the complexes **1–5**, which belong to the family of well-known [Re(CO)₃Cl-(diimine)] species (see Scheme 2).

Compounds **1–5** were synthesized in high yields following the established procedures.^{34,63} In the case of **1** bearing ligand **L1**, the chloride ion was substituted for the cyanide by reacting **1** with a stoichiometric amount of AgCN. Molecular structures of crystallographically characterized complexes **1**, **1-CN**, **2** and **5** are shown in Figure 3 and Figures S5 and S6; the relevant experimental details and selected bond distances and angles given in Tables S1 and S2.

The rhenium ions in these complexes adopt a pseudo-octahedral coordination geometry typical for the related tricarbonyl diimine species, with the N(1)–Re(1)–N(2) angles ranging from 73.95 to 74.25°. The steric hindrance introduced by the bulky phenanthrene moiety is expected to cause a strong repulsion between the equatorial C(2)O(2) ligand and the aromatic H–C group. This results in a significant displacement of the metal center from the plane of polycyclic NN' motif

Scheme 2. Synthesis of Complexes **1–5**^a



^aReagents and conditions: (a) EtOH, reflux, 5 h, N₂; (b) AgCN, MeCN, reflux, 3 h, N₂.

(Figure 3); similarly to compounds with benzoquinoline ligands,⁶⁴ the dihedral angles between the planes of the Re(1), C(1), and C(2) atoms and of the imidazolyl ring are equal to 34.3° (**1**), 41.6° (**1-CN**), 27.5° (**2**), and 34.8° (**5**). In addition, the observed distortions systematically lead to the elongation of the Re(1)–N_{imi}(1) bonds with respect to Re(1)–N_{py}(2) distances (Table S2), which is in contrast to congener Re(I) complexes with pyridyl-imidazole ligands.^{65–67}

Not surprisingly, compounds **1**, **1-CN**, **2**, and **5** display extensive π – π , π –C \equiv C, and CH– π intermolecular interactions (Figures S5 and S6), which essentially influence the crystal packing and might further increase the angle between the diimine backbones and the equatorial planes of the complexes, simultaneously inducing some curvature of the polyaromatic systems.

The spectroscopic data recorded for complexes **1–5** and **1-CN** in solution are compatible with the structures depicted in Scheme 2 and the results of the XRD analysis. The IR spectra of chloro tricarbonyl species **1–5** in the CO stretching region are nearly identical and show three strong bands at ca. 2025, 1922, and 1895 cm^{–1}, which correspond to *fac*-M(CO)₃ fragments lacking 3-fold symmetry.^{43,68} The lower energy CO vibrations for **1-CN** are somewhat shifted to higher frequencies (2024, 1926, and 1914 cm^{–1}), which can be attributed to the substitution of the Cl[–] for the CN[–] ligand with a stronger π -accepting character.

The ESI-MS of **1–5** and **1-CN** reveal the signals [**1** + Na]⁺, [(**1-CN**) + Na]⁺ and [(**2–5**) + Cl][–]/[(**2–5**) + HCOO][–] ions with the isotopic patterns, which fit completely the calculated patterns (Figure S7). The ¹H NMR spectra of these complexes contain well-resolved sets of resonances, which indicate a stereochemically rigid molecular arrangement under ambient conditions. The complete illustrative assignment, performed for **2** on the basis of the ¹H–¹H COSY and NOESY experiments (Figure S8), confirms that the solid-state structure remains unchanged in solution, including the preferential orientation of the imidazolyl-*N*-connected phenylene ring due to the restricted rotation around the N(3)–C₆H₄ bond.

Photophysical Properties and Theoretical Analysis. Ligands **L1–L5.** Compounds **L1–L5** contain extended aromatic motifs (phenanthrene (phen) and secondary

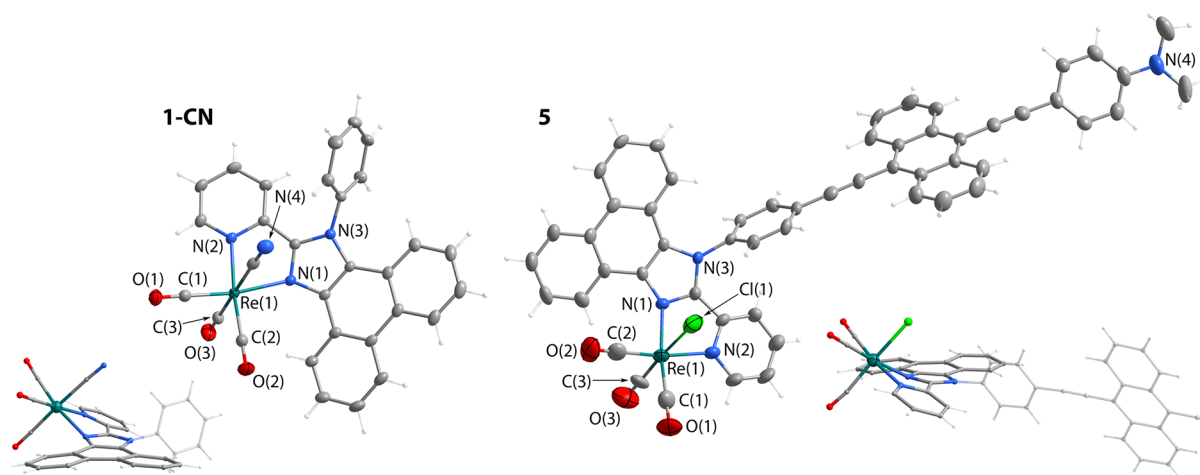


Figure 3. Molecular views of complexes **1-CN** and **5** (thermal ellipsoids are shown at the 50% probability level).

anthracenyl (an) chromophores), the electronic properties of which define their optical behavior and therefore substantially differentiate **L1/L2**, **L3**, and **L4/L5**. The UV–vis spectra for **L1** and **L2** in dichloromethane solution are very much alike and display absorption bands in the range 250–360 nm (Table 1

Table 1. Experimental and Calculated Electronic Absorption Data for **L1** and **L3–L5**

	exptl		calcd		MO configuration, % contribution
	λ , nm	ϵ , M ⁻¹ cm ⁻¹	λ , nm	f	
L1	362	13000	343	0.76	HOMO → LUMO, 94
	330	17000	319	0.04	HOMO → L+1, 83
	261	58000	284	0.09	H-1 → LUMO, 37; HOMO → L+2, 30
L3	425	20000	447	0.62	HOMO → LUMO, 99
	402	22000			
	362	20000	343	0.75	H-1 → L+1, 95
L4	464	12000	529	0.44	HOMO → LUMO, 94
	409	1200	431	0.32	H-2 → LUMO, 94
	363	26000	343	0.73	H-1 → L+1, 95
L5	490	52000	561	1.44	HOMO → LUMO, 99
	363	20000	355	0.25	HOMO → L+2, 91

and Figure S9), corresponding to the π – π^* _{phen} transitions in the aromatic systems, whereas in the case of **L3** the presence of the anthracene moiety results in the appearance of additional longer wavelength absorptions (380–430 nm). Ligands **L4** and **L5**, functionalized with electron-donating –NR₂ groups, expectedly display broad bathochromically shifted bands (470 and 490 nm) attributed to the intramolecular charge transfer.

According to TD-DFT calculations (using PBE0 hybrid density functional taking into account dichloromethane solvent with the C-PCM method), the predicted lowest energy excitations $S_0 \rightarrow S_1$ for **L1** and **L3–L5** are mainly HOMO → LUMO in character (Table 1). For **L1**, it involves phenanthrene-localized $\pi \rightarrow \pi^*$ _{phen} transition mixed with phenanthrene → pyridyl charge transfer, LC/ILCT (Figure 4). In **L3** both the HOMO and LUMO are located on the ethynyl-anthracene fragment with some participation of the phenylene spacer (Figure S10). For **L4** and **L5** the HOMO is substantially delocalized over the entire anthracene-containing chromophore (Figure 4 and Figure S10), which leads to a

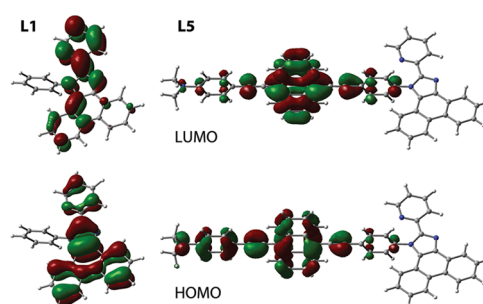


Figure 4. Frontier molecular orbitals for **L1** and **L5**.

visible charge transfer (ILCT) as a result of the $S_0 \rightarrow S_1$ transition. Computationally assessed absorptions (Table 1) correlate rather well with experimental data for **L1** and **L3**, which feature $\pi\pi^*$ character of transitions. However, for CT compounds **L4** and **L5** the energies of $S_0 \rightarrow S_1$ transitions are considerably underestimated.

Compounds **L1** and **L2** exhibit nearly identical violet-blue photoluminescence in solution (Figure 5 and Table 2), which is

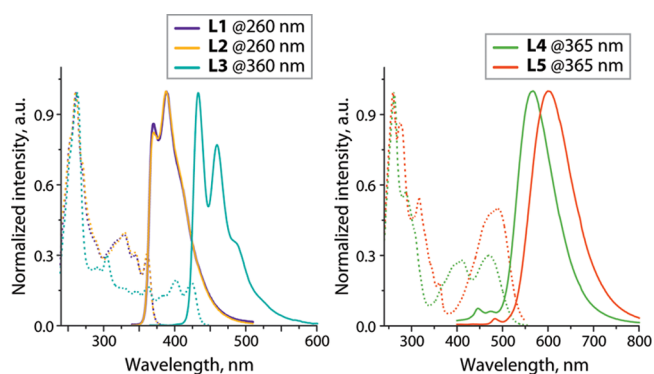


Figure 5. Normalized excitation (dotted lines) and emission (solid lines) spectra of **L1–L5** (CH₂Cl₂, 298 K).

insensitive to molecular oxygen (³O₂) and has a short lifetime of 1.9 ns that indicates its singlet origin. The emission bands are vibronically structured (ν ca. 1250 cm⁻¹), showing no effect of the bromide substituent in **L2**, which is in accordance with the ¹ $\pi\pi^*$ _{phen} nature of the excited state, dominated by the orbitals of the phenanthroimidazole system. Both the absorption and

Table 2. Emission Spectral Data for L1–L5 (298 K, Aerated CH₂Cl₂)

	$\lambda_{\text{em}}, \text{nm}^a$	$\Phi, \%^a$	τ, ns	$k_r, \text{s}^{-1}{}^b$	$k_{\text{nr}}, \text{s}^{-1}{}^c$
L1	370, 388	37	1.9 ± 0.1	1.9 × 10 ⁸	3.3 × 10 ⁸
L2	370, 388	22	1.9 ± 0.1	1.2 × 10 ⁸	4.1 × 10 ⁸
L3	433, 459, 486	65	3.3 ± 0.2	2.0 × 10 ⁸	1.1 × 10 ⁸
L4	446w, 475w, 566	52	2.1 ± 0.1 (446 nm); 1.4 ± 0.1 (566 nm)	3.7 × 10 ⁸	3.4 × 10 ⁸
L5	484w, 602	92	2.6 ± 0.1 (484 nm); 3.8 ± 0.2 (602 nm)	2.4 × 10 ⁸	2.1 × 10 ⁷

^a λ_{ex} 260 nm (L2, L3), 360 nm (L3), 365 nm (L4, L5). ^b k_r values were estimated by Φ/τ_{obs} . ^c k_{nr} values were estimated by $(1 - \Phi)/\tau_{\text{obs}}$.

fluorescence spectra of L1 and L2 are very similar to those of 1,2-diphenyl-1*H*-phenanthro[9,10-*d*]imidazole and the derivatives,^{69,70} which supports the given assignment.

The emission band of L3 is substantially red shifted and looks essentially the same as the fluorescence profiles of phenyl-ethynyl-anthracene and the related anthracene-based compounds.^{71,72} This observation correlates with the results of a theoretical analysis (Figure S10), which points to a major contribution of the anthracene moiety into the lowest-lying S₁ state of $\pi\pi^*_{\text{an}}$ nature. Notably, the congener dye bearing an anthracenyl unit at the N1-phenylene spacer of diphenyl-phenanthroimidazole⁷³ shows a different electronic structure with the HOMO and LUMO distributed over the phenanthrene and anthracene fragments, respectively.

Ligands L4 and L5 display emissions with observed lifetimes of several nanoseconds and intensities being insensitive to the presence of molecular oxygen that corresponds to prompt fluorescence. In contrast to L1–L3, compounds L4 and L5 containing pendant amine groups display structureless emission bands of considerably lower energy (Table 2 and Figure 5). These variations in luminescence characteristics indicate crucial changes in the character of the electronic transitions, which are associated with ILCT arising from the donor–acceptor (R₂N– π -imidazole) molecular structure of L4 and L5 (Figure 4 and Figure S10). Consequently, these dyes show strong fluorescence solvatochromism (Table 3, Figure 6, and Figure S11). Increasing polarity of the solvent (cyclohexane < toluene < dichloromethane < dimethylformamide) results in the bathochromic shift of the major emission band maximum to 2845 cm⁻¹ (L4) and 4853 cm⁻¹ (L5). The lowest energy absorptions are visibly less influenced by the variation of the solvent, which corresponds to the trends typical for charge-transfer luminophores.^{74,75} For both fluorophores the highest emission intensity was determined in dichloromethane

solutions, with quantum yields Φ_{em} reaching 52% and 92% for L4 and L5, respectively. The optical and electronic properties of L5 are close to those of the Me₂N–C₆H₄–C₂–anthracenyl–C₂–C₆H₄–X chromophore (X = electron-withdrawing group),^{76,77} confirming a negligible participation of phenanthroimidazole in the observed electronic transitions for L5. A severe drop in Φ_{em} for L5 in a polar solvent (DMF, Φ_{em} = 7%) is comparable to that observed for this bipolar diethynyl-anthracene congener⁷⁶ and is in line with a larger Stokes shift that implies more explicit geometry distortions of the S₁ state and, consequently, more efficient nonradiative relaxation processes.

The emission energies of L4 and L5 show a linear dependence of the medium dielectric constant, which can be conventionally varied by using mixtures of two different solvents (e.g., toluene/CH₂Cl₂, Figure 6 and Figure S11). This type of dependence is common for systems with photoinduced ILCT where stabilization of charge separated (i.e., polarized) excited state by means of dipole (solute)–dipole (solvent) interactions accounts for the red shift of emission in a polar environment.^{34,74,76,78} A Lippert–Mataga analysis reveals satisfactory linear correlation of the Stokes shift with the solvent polarity (see Figure S12 and the accompanying calculations), from which differences in the electric dipole moment between the S₀ and S₁ states ($\Delta\mu$) for L4 and L5 were found to be 29 ± 5 and 44 ± 8 D, respectively. These values correlate well with those obtained for donor–acceptor species with comparable linear dimensions.^{75,78}

In addition to the main low-energy ILCT emission band, it is possible to distinguish weak high energy signals in the spectra of L4 and L5 (measured from multiply recrystallized samples to exclude the impurities), which are most clearly seen in DMF solutions (Figure 6 and Figures S11 and S13). It should be noted that the increase in HE/LE intensity ratio for L5 in DMF is primarily ascribed to the decrease in LE charge-transfer emission. The difference in the excitation spectra, monitored at the HE and LE bands (Figure S13), suggests two independent emissive states, which are not exceptional for donor–acceptor compounds.^{78–80} The structured profile of the HE emissions may be ascribed to anthracene-centered $\pi\pi^*$ transitions, which lack charge-transfer character. The corresponding excitation patterns for HE bands (Figure S13) are reminiscent of those for L3 and the related compounds⁷² and reveal a red shift typically found for diethynyl anthracene derivatives in comparison to the monosubstituted species. In accordance with the suggested assignment, the energies of HE bands demonstrate insignificant solvatochromic dependence due to an expectedly smaller change in the dipole moment upon $\pi\pi^*$ excitation.

Table 3. Photophysical Data for L4 and L5 in Different Solvents

	solvent	$\lambda_{\text{abs}}, \text{nm}$ ($\epsilon, 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}, \text{nm}$	$\Phi, \%^b$	τ, ns (aer)
L4	cyclohexane	260 (11.2), 310 (3.6), 344 (2.6), 363 (2.6), 409 (0.8), 472 (0.9)	440w, 503	41	<i>c</i>
	toluene	314 (5.9), 345 (4.3), 364 (3.9), 409 (1.2), 470 (1.3)	443w, 531	47	1.4 (443 nm); 8.7 (531 nm)
	CH ₂ Cl ₂	262 (13.5), 311 (5.6), 344 (3.6), 363 (2.6), 409 (1.2), 464 (1.2)	446w, 475w, 566	52	2.1 (446 nm); 1.4 (566 nm)
	DMF	312 (6.4), 343 (3.8), 362 (2.9), 411 (1.4), 465 (1.4)	444w, 472w, 587	38	3.9 (444 nm); 1.4 (587 nm)
L5	cyclohexane ^a	261 (17), 268 (15), 316 (6), 344 (3), 363 (3), 459 (5)	509, 542	64	<i>c</i>
	toluene	319 (5.8), 364 (2.7), 471 (4.9), 490 (4.9)	539	77	2.5 (539 nm)
	CH ₂ Cl ₂	261 (12.4), 273 (9.8), 318 (5.9), 363 (2.0), 471 (4.9), 490 (5.2)	484w, 602	92	2.6 (484 nm); 3.8 (602 nm)
	DMF	319 (6.0), 362 (2.0), 473 (4.6), 495 (5.3)	484mw, 518w, 676	7	2.8 (484 nm); 3.2 (671 nm)

^aExtinction coefficients in cyclohexane are estimated approximately due to low solubility of L5. ^b λ_{ex} 365 nm. ^cCould not be determined accurately due to low solubility.

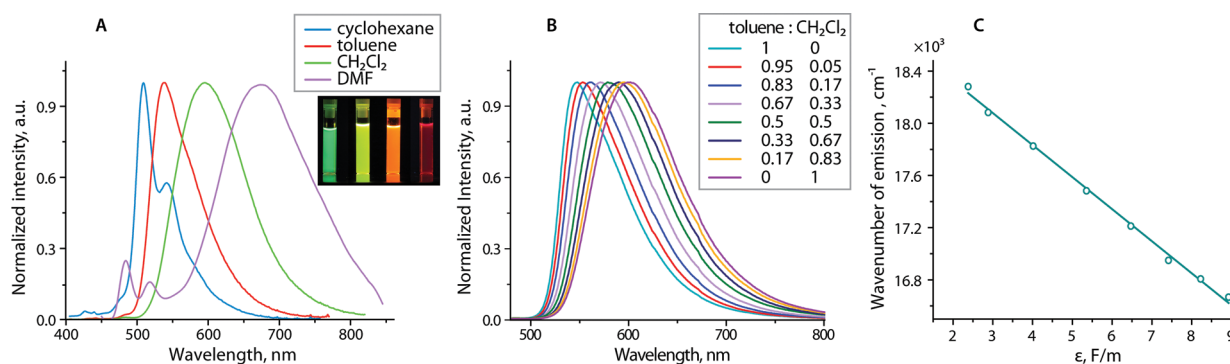


Figure 6. Normalized emission spectra of **L5** at 298 K: (A) in various solvents, with the inset showing their visual appearance under UV light (λ 365 nm); (B) in toluene– CH_2Cl_2 mixtures; (C) dependence of the emission energy on polarity (dielectric constant) of toluene– CH_2Cl_2 solutions, $R^2 = 0.996$.

Response to Protonation. The electron-donating N-functions of **L1–L5** can be easily protonated, which substantially affects the photophysical characteristics of these compounds. Adding an excess of trifluoroacetic acid to solutions of **L1** and **L2** causes an immediate appearance of a yellow-greenish color and changes the emission from deep blue (λ_{em} 370, 388 nm) to vivid green due to the emergence of two broad bands maximized at ca. 413 and 517 nm (Figure 7 and Figure S14).

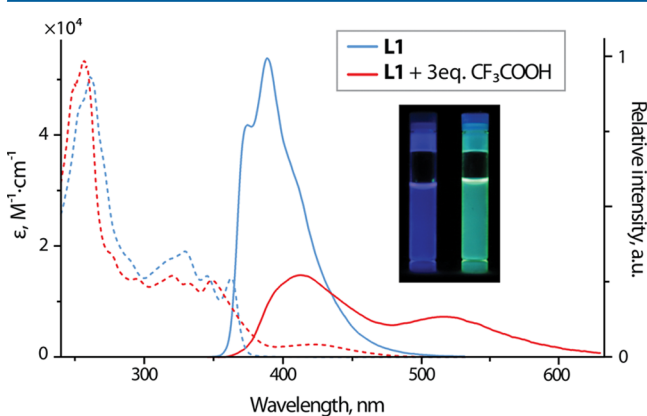


Figure 7. Effect of protonation on the absorption and emission spectra of **L1** ($c = 5.8 \times 10^{-5}$ M, CH_2Cl_2 , 298 K). The inset shows the visual appearance of **L1** (left) and $[\text{L1} + \text{H}]^+$ (right) under UV light (λ 365 nm).

The corresponding ^1H NMR spectra (Figure S15) indicate that protonation most probably occurs on the diimine (pyridyl-imidazole) part of the molecule, which is reflected by the large low-field shift of the pyridyl H(9) atom as a result of electronic deshielding, analogously to the coordination-induced shift observed for rhenium complexes (Figure S8). Protonation of the pyridinium fragment is expected to stabilize the LUMO level that activates the $\text{ILCT}_{\text{phen} \rightarrow \text{py}}$ excited state and decreases the energies of both absorption and emission. Reminiscent variations in the optical characteristics due to an emission switch to the ILCT mode have been recently described for a phenanthro-imidazole probe for formaldehyde.⁸¹ Treatment of **L3** and **L4** with the acid leads to a large decrease in fluorescence intensity without a considerable change in emission energy (Figure S14). This effect might be attributed to the increased electron-withdrawing ability of the diimine motif that facilitates photoinduced electron transfer from the

anthracene-based donor. The basicity of the terminal $\text{Ph}_2\text{N}-\text{C}_6\text{H}_4-$ group in **L4** is expected to be much lower than that of pyridyl and dimethylaminophenyl functions (in **L5**) ($\text{p}K_{\text{a}}$ values of conjugate acids of pyridine, dimethylaniline, and Ph_3N in acetonitrile are 12.53, 11.43, and 1.3, respectively^{82,83}); therefore, protonation of the diphenylamine group in **L4** is not likely to occur.

In the case of **L5**, however, the high proton affinity of the aniline $\text{Me}_2\text{N}-\text{C}_6\text{H}_4-$ function is evidently responsible for reversible switching of the optical properties. In acidic medium the long-wavelength absorption (492 nm) is gradually decreased, which is accompanied by the simultaneous growth of the adjacent blue-shifted band with a clearly distinguishable isosbestic point at 476 nm (Figure 8). Accordingly, the low-

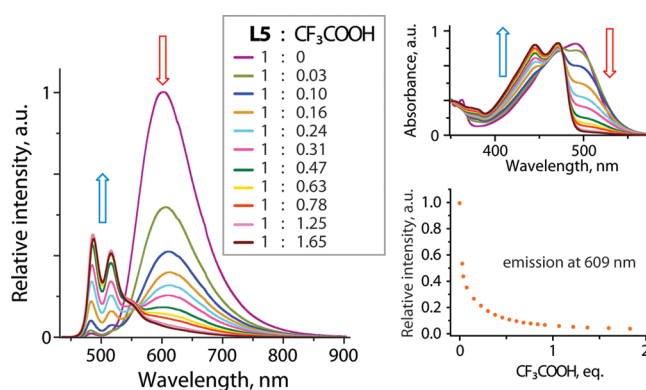


Figure 8. Effect of protonation on the absorption and emission spectra of **L5** ($c = 10^{-5}$ M, CH_2Cl_2 , 298 K).

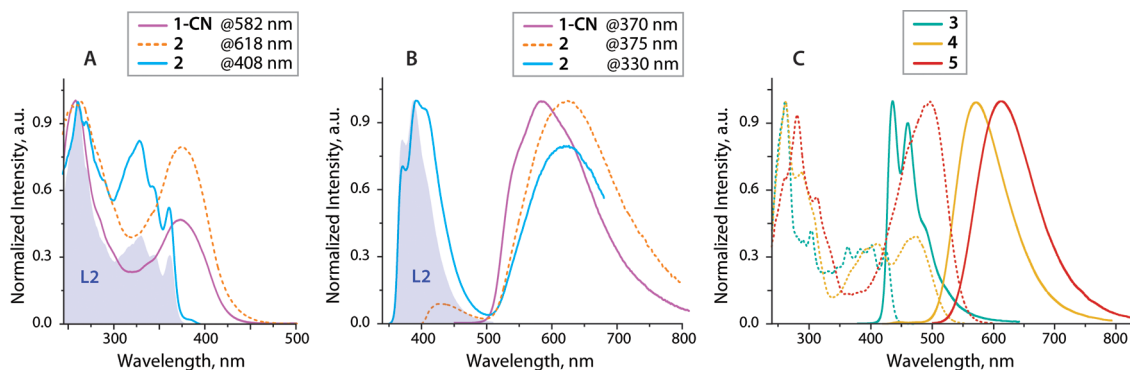
energy broad charge-transfer emission (602 nm in CH_2Cl_2) is replaced by the high-energy structured band (487 nm) that is assigned to $\pi \rightarrow \pi^*_{\text{an}}$ anthracene-centered transitions. Addition of a base (e.g., triethylamine, DBU) restores the original orange ILCT fluorescence.

Rhenium(I) Complexes. The photophysical properties of compounds **1–5** and **1-CN** are summarized in Table 4. The absorption spectra of **1**, **1-CN**, and **2** in dichloromethane solution (Figure S16) display high-energy (HE) bands at ca. 260 nm, which are primarily assigned to $^1\pi \rightarrow \pi^*_{\text{phen}}$ transitions within the aromatic system of the phenanthro-diimine fragments. The longer wavelength weaker absorptions with maxima at ca. 375–378 nm ($\epsilon = (2.1\text{--}2.3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and tails up to 450 nm are not observed for the free ligands and apparently correspond to the spin-allowed $^1\text{ML}'/\text{LCT}$ ($\text{L}' = \text{Cl}/$

Table 4. Photophysical Properties of Complexes 1–5 and 1-CN in Solution (Degassed CH₂Cl₂, 298 K)

	λ_{abs} , nm (ϵ , 10 ⁴ M ⁻¹ cm ⁻¹)	λ_{em} , nm	Φ , % ^a	τ_{obs} , ns	k_r , s ⁻¹ ^b	k_{nr} , s ⁻¹ ^c
1	259 (5.1), 377 (2.1)	369, 392, 408, 616	2 (616 nm)	2.6 ± 0.1 (392 nm); 186 ± 9 (616 nm)	1.1 × 10 ⁵	5.3 × 10 ⁶
1-CN	258 (5.8), 375 (2.2)	582	20	3550 ± 250	5.6 × 10 ⁴	2.3 × 10 ⁵
2	259 (6.1), 378 (2.3)	371, 392, 407, 624	2 (624 nm)	2.1 ± 0.1 (405 nm); 142 ± 7 (624 nm)	1.4 × 10 ⁵	6.9 × 10 ⁶
3	263 (14.1), 303 (2.9), 384 (3.4), 403 (3.4), 427 (2.5)	436, 460, 486(sh)	3	4.1 ± 0.2	7.3 × 10 ⁶	2.4 × 10 ⁸
4	262 (18.8), 384 (4.9), 470 (2.1)	572	10	4.5 ± 0.2	2.2 × 10 ⁷	2.0 × 10 ⁸
5	260 (15.2), 380 (3.9), 478 (6.5), 493 (6.4)	614	22	2.7 ± 0.1	8.1 × 10 ⁷	2.9 × 10 ⁸

^a λ_{ex} 365 nm. ^b k_r values were estimated by Φ/τ_{obs} . ^c k_{nr} values were estimated by $(1 - \Phi)/\tau_{\text{obs}}$.

Figure 9. Normalized excitation (A) and emission (B) spectra of 1-CN and 2 (the corresponding spectra of L2 (filled) are shown for comparison) and (C) excitation (dotted lines) and emission spectra (solid lines) of 3–5 (degassed CH₂Cl₂, 298 K).

CN/CO) transitions (i.e., {Re(CO)₃X} → NN ligand, Figure S17 and Table S3), which conforms with earlier theoretical and spectroscopic investigations of [Re(CO)₃X(diimine)] compounds.^{84–88}

The UV–vis absorption patterns of 3–5 are reminiscent of those obtained for free ligands L3–L5. In the low-energy region these complexes feature electronic transitions, which are determined by the anthracene-based chromophores (Figure S18 and Table S3). These bands are only slightly red shifted with respect to those of L3–L5, which contrasts with the coordination response of donor-functionalized dipyrrophenazine^{34,78} and pyridyl-triazole¹⁹ ligands and points to essentially independent electronic behavior of phenanthro-diimine and anthracene motifs. Nevertheless, the ILCT absorptions for 4 and 5 demonstrate a substantial increase in extinction coefficients to 21000 and 64000 M⁻¹cm⁻¹, respectively (cf. 12000 and 52000 M⁻¹cm⁻¹ for L4 and L5). Analogously to the aforementioned compounds 1 and 2, the ML/LCT band at ca. 380 nm is evidently present for 3–5 as well and is clearly visible in the spectrum of 5 (but is absent for L5; Figure S16).

Complexes 1–5 and 1-CN are luminescent at room temperature both in solution and in the solid state (except 3) (see Figure 9 and Figures S19 and S20). In fluid medium 1 and 2 demonstrate dual emission, which is possible to manipulate by varying the excitation wavelength. Selective irradiation into the long-wavelength absorption (λ_{exc} 375 nm) of 1 and 2 results in a predominantly low-energy structureless emission with a maximum at ca. 620 nm ($\Phi_{\text{em}} = 2\%$) and lifetimes of 0.19 (1)/0.14 (2) μs (Table 4); the latter values are comparable to those of other Re(I) diimine tricarbonyl compounds.^{37,38,67,89,90} The intensity of the LE band appreciably decreases in aerated solution, which suggests a triplet origin of the excited state (i.e., ³ML/LCT likely mixed with some ³LC). Higher energy excitation (λ_{exc} 330 nm) results in appearance of an HE band

with a maximum at 392 nm, particularly pronounced for complex 2 (Figure 9B), in addition to low-energy ³CT emission. The vibronic structure (ν ca. 1440 cm⁻¹) of the HE band, its position, and the corresponding excitation spectrum, which are close to those of L1 and L2, point to the ligand-centered ¹LC nature of HE emissions (i.e., fluorescence) that is also evidenced by short lifetimes of 2.1–2.6 ns.

In this respect it should be noted that Re(I) diimine complexes, dually emissive in solution under ambient conditions, are rare. Thus, two ³MLCT emissive states with nearly the same energies arising from different conformers were proposed for [Re(Me₂bipy)(CO)₂(PR₃)₂]⁺ compounds.⁹¹ Two clearly resolved emission bands assigned to ¹ $\pi\pi^*$ (HE) and ³ $\pi\pi^*$ (LE) origins were observed for the family of [Re(NN)-(CO)₃Cl] species (NN = pyridylimidazo[1,5-*a*]pyridine ligands), though at a low intensity of less than 0.3%.^{92,93} Ultimately, dual luminescence from $\pi\pi^*$ (HE) and MLCT (LE) levels was suggested for dirhenium metallacycle⁹⁴ and [Re(NN)(CO)₃Cl] compounds (NN = dipyrrophenazine-based ligands),⁹⁵ while for [Re(NN)(CO)₃(L)]⁺⁰ species both ¹ILCT and ³MLCT excited states were found to undergo radiative relaxation in solution.⁴⁴ In addition, a few complexes bearing pendant fluorophores exhibit singlet and triplet luminescence from two different spatially separated emissive centers.^{39,43,96}

The unconventional behavior of 1 and 2 can be tentatively rationalized by the qualitative energy level diagram (Figure 10). It is assumed that, due to the presence of a polyaromatic phenanthrene system, irradiation of these complexes with λ_{exc} 330 nm can optically populate both ligand-centered ¹ $\pi\pi^*$ _{phen} and ¹ML/LCT states, which are normally not mixed due to the large energy separation⁸⁷ and thus can potentially relax following independent pathways. The singlet charge-transfer

data involves electron transfer from the electron-rich chromophore to the photoexcited $\{\text{Re}^{\text{II}}(\text{diimine})\}$ motif; such a process is not exceptional for rhenium(I) luminophores, and its probability depends on the properties of the diimine ligand.^{43,108} The described photophysical behavior of **4** and **5** clearly contrasts with optical characteristics of the majority of rhenium(I) diimine compounds, which predominantly exhibit triplet emission or the formation of the intraligand dark triplet states.^{32–36}

CONCLUSIONS

We have developed the family of readily accessible diimine ligands based on a coordinating pyridyl-phenanthroimidazole motif (**L1**, **L2**), which was functionalized with electron-rich anthracene-based units to give bichromophoric molecules **L3**–**L5**. The optical properties of ligands **L1** and **L2** are defined by $\pi\pi^*/\text{CT}$ (phenanthrene \rightarrow pyridyl) electronic transitions, whereas for **L3**–**L5** they are localized in the anthracene motif. The donor–acceptor architecture of **L4** and **L5** enables efficient low-energy intramolecular charge-transfer transitions (maximum λ_{abs} 490 nm with tails below 550 nm for **L5** in CH_2Cl_2). The title compounds are luminescent in solution, showing moderate to high quantum efficiencies, and cover a wide range of emission wavelengths from violet to orange-red ($\Phi_{\text{em}} = 22$ –92%, λ_{em} 370–602 nm in CH_2Cl_2). The charge-transfer character of emission for **L4** and **L5** determines their pronounced fluorescence solvatochromism. The presence of electron donor groups (pyridyl and dimethylaminophenyl) susceptible to protonation allows for reversible switching of emission parameters by affecting the charge-transfer processes. Ligands **L1**–**L5** easily get coordinated to the rhenium(I) center, forming the corresponding complexes of the general composition $[\text{Re}(\text{CO})_3\text{X}(\text{diimine})]$ ($\text{X} = \text{Cl}$, **1**–**5**; $\text{X} = \text{CN}$, **1-CN**). Compounds **1** and **2** demonstrate dual fluorescence–phosphorescence arising from the same organic fragment that is a rare behavior for rhenium(I) luminophores. This phenomenon is tentatively attributed to the excitation-dependent population of poorly coupled $^1\pi\pi^*$ and ^3CT excited states, which undergo independent radiative relaxation leading to high- and low-energy emission bands. Changing the chloride for cyanide has a pronounced effect on luminescence intensity that reveals 10-fold increase in **1-CN** in comparison with **1**.

Photoemission of complexes **3**–**5** is dominated by the intraligand transitions, only slightly perturbed by the presence of the metal ion. The lack of phosphorescence originating from $^3\text{ML/LCT}$ or $^3\text{IL}(\text{phenanthrene})$ might be explained by the triplet energy transfer to the nonemissive state of the anthracene moiety. Moderately intense intraligand fluorescence detected for **4** and **5** is drastically different from the properties of the major part of the known rhenium(I) luminophores.

The reported ligands, showing intense absorption and emission bands in a wide range of the visible spectrum, are thought to be suitable for the preparation of a variety of photofunctional coordination metal complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00422.

Preparation of the ligands **L1**–**L5**, crystallographic and computational details, and ESI-MS, NMR, and additional photophysical data (PDF)

Accession Codes

CCDC 1824098–1824103 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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