

Computer-aided design of short-lived phosphorescent Ru(II) polarity probes

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ABSTRACT

Fluorescent polarity probes are usually based on intramolecular charge transfer excited states of selected dyes, the behavior of which in different solvents is traditionally rationalized by the well-known Lippert-Mataga treatment of the “general solvents effect”. Less often transition metal coordination complexes are used as luminescent probes, even though the spectroscopic properties of these dyes are usually dependent on the environment. This is the case of Ru(II) polypyridyls, which are good candidates to develop robust sensitive polarity probes because of their lowest-lying metal-to-ligand charge transfer triplet emissive state, provided their chelating ligands structure is judiciously tuned. The aim of this work has been to design a computational strategy to forecast the behavior of polarity-sensitive Ru(II) complexes without the need to prepare a large set of candidates. In particular, we have analysed a number of complexes derived from $[\text{Ru}(\text{bpy})_3]^{2+}$ by introducing different pairs of substituents in the 4,4' positions of one of the three equivalent 2,2'-bipyridine (bpy) moieties. In this way, we have investigated if a direct relationship may be established between the electronic features of the substituent and the Stokes shift sensitivity to the solvent polarity. Our computational data satisfactorily agree with our experimental results, but they demonstrate that only by explicitly performing the calculation of the Stokes shift in different media for each candidate, it is possible to select the best Ru(II) dyes to be used as polarity probes.

KEYWORDS: Polarity probes; Ru(II) polypyridyl complexes; DFT calculations; Luminescence; Solvent effects

1. Introduction

Polarity measurements of the solvent media or of the materials are of high interest in numerous fields. In particular, fluorescent organic dyes have been widely used as molecular probes of the local environment. The basis is that the probe luminescence features (i.e. position and intensity of its maximum, vibronic fine structure, emission quantum yield, emission lifetime and polarization) are dependent on the direct environment around the probe [1]. In Biology, for example, micropolarity probes are much employed for distinguishing and imaging different microenvironments: although the typical solvent in biological systems is water, there are significant variations of polarity within proteins, vesicles, cells and tissues [2]. In addition, polarity probes may also detect biomolecular interactions [3]. Other important applications of environmentally-sensitive dyes are monitoring hydrocarbons in water (e.g. fuel leaks) [4] or, conversely, water in non-polar solvents of industrial processes, e.g. during solvents and chemicals production or purification [5]. The use of optical sensors to monitor micropolarity has particular advantages, especially because it allows easy miniaturization (with the use of optical fibers), imaging, and unbeatable spatial resolution down to the nanosize [6].

When designing polarity probes, one major complication arises from the loose definition of “polarity”. While for an isolated molecule it generally refers to the internal distribution of its electron density, the interaction between molecules is more complex to describe. In particular, for a minor (solute, probe) and a major component (solvent, surroundings in materials), there are always non-specific interactions that depend mainly on the intrinsic polarity of the solute and on the relative permittivity (ϵ_r) and refractive index (n) of the solvent [1b]. In addition, there may be specific interactions such as hydrogen bonding [7], preferential solvation [8], acid-base chemistry [9], and induction of charge-transfer [10].

From the different theoretical and experimental studies of the effects of the environment on the luminescence of organic molecules, numerous mathematical relationships have been developed [1]. Most of them are based on a linear correlation between the difference in wavenumbers separating the absorption and fluorescence maxima of the luminophore (Stokes shift, $\Delta\nu = \nu_a - \nu_e$), and a property of the solvent related to its “polarity”. The most popular is probably the relationship found by Lippert [11] and Mataga [12] for a model assuming that the solvent is a continuous medium and the solute is into a “spherical cavity” within it (eq 1),

$$\Delta\nu = \frac{1}{4\pi\epsilon_0} \frac{2}{\hbar c a^3} (\mu_e - \mu_g)^2 \Delta f + \text{const.} \quad [1]$$

where a is the cavity radius of the reaction field model¹³ and Δf is the solvent orientation polarizability given by eq 2.

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad [2]$$

Eq 1 reveals that the Stokes shift increases linearly with increasing Δf , and that the slope is positive and proportional to the square of the difference in dipole moment between the ground and the excited state. Due to its simplicity, the Lippert-Mataga (L-M) relationship has been widely used. Pronounced solvatochromic effects on the electronic emission band can be produced by various excited state processes, being intramolecular charge transfer (ICT) the most common one. The main feature of ICT dyes is the presence of electron-withdrawing and electron-releasing moieties in specific positions of the molecule. Following absorption of a photon, an electron is transferred from the donor to the acceptor moieties in a so-called “push-pull” mechanism, leading to transient charge separation within the molecule and to an important increase of the dipole moment. Therefore, polarity effects are particularly noticeable on the luminescent properties of those dyes due to the large variation of dipole moment between the ground and the electronically excited species, leading to dramatic differences in their solvation (or interaction with the microenvironment) after the photon absorption.

Unfortunately, the simplicity of the L-M model does not account properly for this type of systems. Moreover, its applicability is also limited because all the solvent-solute *specific* interactions are completely left out. To overcome it, many authors have developed empirical ways to evaluate the polarity of the microenvironment. For instance, Zelinskii et al. studied the solvatochromism of 4-amino-*N*-methylphthalimide, the fluorescence of which red-shifts with the solvent polarity [14]. Dimroth et al. set the so-called $E_T(30)$ scale, based on the energy of the longest-wavelength solvatochromic absorption

band of a pyridinium *N*-phenoxide betaine dye [15]. Nakajima has reported the effect of polarity on the vibronic structure of the fluorescence spectrum of pyrene [16], later used by Dong and Winnik for experimental solvent polarity evaluation with the so-called “Py” scale [17]. Amongst all these methods, luminescence measurements have many advantages compared to absorption determinations because of the higher sensitivity and selectivity of the former. These features are essential for fluorescence-based imaging, single-molecule, nanoprobe and quantitative analysis.

Optical probes have also been used for evaluating the “empirical polarity” of many different environments. The $E_T(30)$ parameter has been determined for as many as 270 solvents [18], as well as for solvent mixtures, ionic liquids, surface of solids, and microheterogeneous systems, e.g. surfactants and polymers [19]. The Py scale has been particularly useful for investigating micelles [20], polymers [21], proteins [22], and biological membranes [23]. However, despite all the progress in the field, these methods have also weaknesses. First of all, as they are empirical, they cannot be used for obtaining parameters such as the dipole moment or the hydrogen donating-accepting features of the immediate environment around the probe. Secondly, the estimated polarity degree is strongly dependent on the probe molecule [1b]. Additional polarity scales have been developed, trying to combine the strengths of the Lippert-Mataga and the empirical methods. An extensive review of the work carried out in this area has been produced by Reichardt and Welton [1b].

The absorption and emission features of transition metal complexes are dependent on the microenvironment polarity as long as their lowest lying electronic excited state has charge transfer (CT) nature [10]. Therefore, these molecules should be versatile polarity probes because the metal center, its oxidation state, and the nature and number of ligands allow a fine tuning of their spectroscopic properties. In particular, the readily accessible long-lived (triplet) metal-to-ligand CT ($^3\text{MLCT}$) excited state of the highly photostable ruthenium(II) polypyridyl dyes may be a good candidate to develop robust polarity probes if the underlying factors that influence their response are mastered. These popular pseudooctahedral coordination complexes show well-separated ($> 150 \text{ nm}$) absorption and emission maxima in the visible, a $^3\text{MLCT}$ luminescent state with a rather long lifetime ($\geq 5 \mu\text{s}$), moderate quenching **rate constant** by molecular oxygen (ca. 10 times as slow as that of fluorescent organic probes and about 100 times less efficient than that of typical phosphors), and their (photo)physical features can be finely tuned by a judicious selection of their chelating ligands [24]. The effect of the microenvironment polarity on the photophysics of some Ru(II) complexes has been studied [10,25], mostly on the highly symmetric forefather of the family, the $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine).

Our aim has been to design efficient luminescent polarity probes, able to report information about their microenvironment, that can be interrogated with the very same optoelectronic instrumentation currently widespread for O₂ sensing in industrial, environmental and clinical fields [24]. Such instrumentation typically uses luminescence lifetime measurements of the indicator dye, normally Ru(II) polypyridyls or porphyrins, most often based on the emission phase shift monitoring. To be able to sense the polarity around the Ru(II) dye, we must avoid or slow down the interligand electron hopping in the emissive ³MLCT state that occurs after the initial electronic transition and very fast intersystem crossing to this state. In particular, we should try to confine as much as possible the photoexcited electron to one of the ligands in order to maximize the dipole moment change in the emissive (triplet) excited state, increasing the probe response to environmental changes. Electron localization can be achieved by replacing one of the three equivalent bpy moieties of [Ru(bpy₃)]²⁺ with another ligand of the 2,2'-bipyridine family bearing electron withdrawing (EW) groups in the 4,4' positions to yield a significantly lower-lying LUMO (lowest unoccupied molecular orbital) [26]. The selection of the most efficient EW groups for this use will be based on computational results. Moreover, the possibility of selecting different (EW)₂bpy ligands makes this scaffold a suitable one to investigate the effect of the coordination ligands on the response to polarity of those probes. Their quasi-octahedral symmetry resembles a sphere for which the Onsager cavity radius (eq 1) is easy to estimate, in contrast to elongated ICT polarity probe molecules, the ellipsoidal shape of which is usually assumed to study their solvatochromism.

Our approach has been to use general solvent effects but tuned to the specific molecule. The idea is to exploit a computational approach to forecast the behavior of polarity-sensitive Ru(II) complexes without the need to prepare further candidates. The computational study has been extended also to systems with electron-donor substituents in the bpy and related ligands (structures shown in SI) to obtain a more general picture of the potential candidates to be used as polarity probes. Such wide variety of substituted ligands should help to improve their design and to investigate if a direct relationship can be established between the electronic properties of those substituent groups and the Stokes shift variation with the microenvironment polarity around the probe.

2. Experimental

2.1 Materials

2.1.1 Ligands

The polypyridyl ligands 4,4'-dichloro-2,2'-bipyridine (DCIB), 4,4'-dicyano-2,2'-bipyridine (DCNB), and dimethyl 2,2'-bipyridine-4,4'-dicarboxylate (DCBB) were purchased from Fluorochem (Hadfield, UK) and used as received ($\geq 95\%$). HPLC or spectroscopic grade solvents were from VWR, Acros Organics or Sigma-Aldrich.

2.1.2 Luminescent Ru(II) dyes

The starting *cis*-Ru(bpy)₂Cl₂ complex has been synthesized following a literature procedure [27]. The corresponding heteroleptic metal complexes (Figure 1) have been prepared by microwave-assisted synthesis.

[(4,4'-Dichloro-2,2'-bipyridine)bis(2,2'-bipyridine)]ruthenium(II) bis(hexafluorophosphate) (1). *cis*-Ru(bpy)₂Cl₂ (1 eq) and DCIB (1.1 eq) were suspended in a 10 mL 1:1 mixture (v/v) of EtOH and H₂O and placed in a microwave-reaction vessel. The latter was capped and purged for 15 min with +99.99% argon (Contse). Then the mixture was heated at 110 °C for 30 min in a laboratory microwave reactor (Biotage). After cooling to room temperature, the EtOH was removed in a rotary evaporator. To the remaining aqueous solution, a saturated aqueous solution of NH₄PF₆ (Alfa Aesar) was added dropwise to precipitate the sought product as its PF₆⁻ salt. After subsequent vacuum filtration, the collected solid was washed with diethyl ether (3 × 10 mL) and dried at 40 °C under reduced pressure (< 1 mbar). Yield: 85%. ¹H NMR (CD₃CN) δ /ppm; J/Hz: 8.59 (H-3^{Cl-bpy}, dd; ⁴J = 1.9, ⁵J = 0.6); 8.49 (H-3,3'^{bpy}, ddd; ³J = 8.2, ⁴J = 1.5, ⁵J = 0.7); 8.07 (H-4^{bpy}, ddd; ³J = 8.3, ³J = 8.1, ⁴J = 2.5); 8.05 (H-4'^{bpy}, ddd; ³J = 8.3, ³J = 8.1, ⁴J = 2.5); 7.76 (H-6^{bpy}, ddd; ³J = 5.6, ⁴J = 1.5, ⁵J = 0.7); 7.68 (H-6'^{bpy}, ddd; ³J = 5.6, ⁴J = 1.5, ⁵J = 0.7); 7.66 (H-5^{Cl-bpy}, dd; ³J = 5.8, ⁵J = 1.8); 7.46 (H-6^{Cl-bpy}, dd; ³J = 5.9, ⁴J = 0.6); 7.46 (H-5^{bpy}, ddd; ³J = 8.1, ³J = 5.6, ⁴J = 1.5); 7.43 (H-5'^{bpy}, ddd; ³J = 8.1, ³J = 5.6, ⁴J = 1.5). The assignment of its NMR data and those of the other luminescent probes followed the work of Orellana et al. [27]. ESI-MS(+) (*m/z*): Found [M]²⁺ = 318.9 (calc. for RuC₃₀H₂₂N₆Cl₂²⁺ = 319.0); [M]⁺ = 782.9 (calc. for RuC₃₀H₂₂N₆Cl₂PF₆⁺ = 783.0).

[(4,4'-Dicyano-2,2'-bipyridine)bis(2,2'-bipyridine)]ruthenium(II) bis(hexafluorophosphate) (2). The same procedure used for the synthesis of the 4,4'-dichloro analogue was followed in this case. Yield: 49%. ^1H NMR (CD_3CN) δ/ppm ; J/Hz : 9.08 ($\text{H-3}^{\text{CN-bpy}}$, dd; $^4J = 1.8$, $^5J = 0.7$); 8.55 (H-3^{bpy} , ddd; $^3J = 8.3$, $^4J = 1.3$, $^5J = 0.6$); 8.54 ($\text{H-3}'^{\text{bpy}}$, ddd; $^3J = 8.3$, $^4J = 1.3$, $^5J = 0.6$); 8.13 (H-4^{bpy} , ddd; $^3J = 8.3$, $^3J = 7.6$, $^5J = 1.4$); 8.11 ($\text{H-4}'^{\text{bpy}}$, ddd; $^3J = 8.3$, $^3J = 7.6$, $^5J = 1.4$); 7.98 ($\text{H-6}^{\text{CN-bpy}}$, dd; $^3J = 5.9$, $^5J = 0.7$); 7.85 ($\text{H-5}^{\text{CN-bpy}}$, dd; $^3J = 5.9$, $^4J = 1.8$); 7.74 (H-6^{bpy} , ddd; $^3J = 5.6$, $^4J = 1.4$, $^5J = 0.7$); 7.69 ($\text{H-6}'^{\text{bpy}}$, ddd; $^3J = 5.6$, $^4J = 1.4$, $^5J = 0.7$); 7.47 (H-5^{bpy} , ddd; $^3J = 7.6$, $^3J = 5.6$, $^4J = 1.3$); 7.42 ($\text{H-5}'^{\text{bpy}}$, ddd; $^3J = 7.6$, $^3J = 5.6$, $^4J = 1.3$);. ESI-MS(+) (m/z): Found $[\text{M}]^{2+} = 309.9$ (calc. for $\text{RuC}_{32}\text{H}_{22}\text{N}_8^{2+} = 310.0$).

[(4,4'-Dimethoxycarbonyl-2,2'-bipyridine)bis(2,2'-bipyridine)]ruthenium(II) dichloride (3). The same procedure than that employed to prepare the 4,4'-dichloro analogue was followed, except that the organic solvent was removed by freeze-drying so that the metal complex was obtained as its chloride salt. Yield: 94%. ^1H NMR (CD_3CN) δ/ppm ; J/Hz : 9.08 ($\text{H-3}^{\text{Ac-bpy}}$, dd; $^4J = 1.8$, $^5J = 0.7$); 8.94 (H-3^{bpy} , ddd; $^3J = 8.3$, $^4J = 1.3$, $^5J = 0.7$); 8.93 ($\text{H-3}'^{\text{bpy}}$, ddd; $^3J = 8.3$, $^4J = 1.3$, $^5J = 0.7$); 8.16 (H-4^{bpy} , ddd; $^3J = 8.3$, $^3J = 7.6$, $^4J = 1.5$); 8.14 ($\text{H-4}'^{\text{bpy}}$, ddd; $^3J = 8.3$, $^3J = 7.6$, $^4J = 1.5$); 8.03 ($\text{H-6}^{\text{Ac-bpy}}$, dd; $^3J = 5.9$, $^4J = 0.7$); 7.86 ($\text{H-5}^{\text{Ac-bpy}}$, dd; $^3J = 5.9$, $^4J = 1.8$); 7.75 (H-6^{bpy} , ddd; $^3J = 5.6$, $^4J = 1.5$, $^5J = 0.7$); 7.72 ($\text{H-6}'^{\text{bpy}}$, ddd; $^3J = 5.6$, $^4J = 1.5$, $^5J = 0.7$); 7.48 (H-5^{bpy} , ddd; $^3J = 7.6$, $^3J = 5.6$, $^4J = 1.3$); 7.44 ($\text{H-5}'^{\text{bpy}}$, ddd; $^3J = 7.6$, $^3J = 5.6$, $^4J = 1.3$); 4.01 ($\text{CH}_3^{\text{Ac-bpy}}$, s). ESI-MS(+) (m/z): Found $[\text{M}]^{2+} = 342.7$ (calcd for $\text{RuC}_{34}\text{H}_{28}\text{N}_6\text{O}_4^{2+} = 343.0$); $[\text{M}]^+ = 830.9$ (calc. for $\text{RuC}_{34}\text{H}_{28}\text{N}_6\text{O}_4\text{Cl}_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH} = 831.1$).

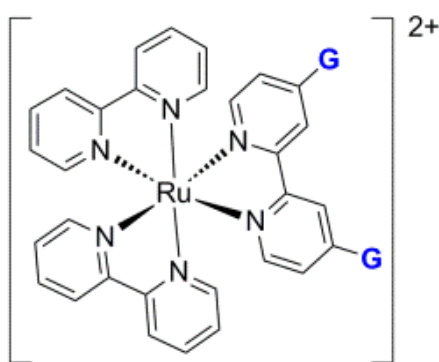


Figure 1. General structure of the luminescent Ru(II) coordination complexes $[\text{Ru}(\text{bpy})_2(\text{G}_2\text{bpy})]^{2+}$ investigated in this work. G stands for the electron-withdrawing Cl, CN or CO_2CH_3 groups of dyes (1), (2) and (3), respectively.

2.2 Spectroscopic characterization

Water was purified with a Millipore Direct-Q3-UV system (Bedford, MA). HPLC-grade solvents were purchased from Sigma-Aldrich Química (Madrid, Spain) and dried over 3 Å molecular sieves for at least one week prior to use. The ^1H -NMR spectra have been obtained at the UCM Central NMR Instrumentation Facilities with a Bruker DPX 300 MHz spectrometer. ESI-MS spectra were recorded at the UCM Central MS Facilities on a LTQ XL linear ion trap mass spectrometer fitted with an electrospray ionization (ESI) sample inlet. UV-VIS absorption spectra were acquired with a Varian Cary 3-Bio (Palo Alto, CA, USA).

Luminescence was measured on a Fluoromax-4TCSPS spectrofluorometer (Horiba, Kyoto, Japan). The dye solutions were analyzed into 1-cm pathlength Suprasil cells (Hellma, Mülheim, Germany). All emission spectra were corrected after subtracting the signal of the pure solvent obtained under the same conditions. The correction curve was obtained with a calibrated irradiance lamp (Oriel Instruments). Emission lifetime measurements were carried out with an Edinburgh Instruments FL-980 TCSPC fluorometer equipped with a Horiba NanoLed-470LH laser diode (<1 -ns 463-nm pulses at 1.0 MHz). Exponential luminescence decays were measured with a 10 or 50 μs window (1024 channels) by accumulating at least 10^4 counts in the peak channel, and emission lifetimes were extracted from the exponential curve fittings using the proprietary Marquardt-Levenberg non-linear least squares fit algorithm (without deconvolution) for stable chi-squared minimization ($\chi^2 < 1.05$ in all cases).

2.3 Computational strategy

The geometries of the S_0 and T_1 states of the Ru(II) complexes have been optimized with the density functional theory (DFT) using the Perdew–Burke–Ernzerhof exchange-correlation functional mixed with 25% exact Fock exchange (PBE0) [30]. The Kohn-Sham orbitals are expanded in a basis set of split valence quality (def2-SVP) [31]. The $S_0 \rightarrow S_1$ absorption energy is calculated with time-dependent DFT in the Tamm-Dancoff approximation [32], whereas the $T_1 \rightarrow S_0$ emission can be determined by standard DFT calculations being the lowest states of the respective spin manifold. Geometry optimizations were performed with the TurboMole 6.6 program package [33] and TD-DFT calculations with Gaussian 09 [34].

The solvent effects are incorporated in the calculations through the Conductor-like solvent model (COSMO) [35] in TurboMole, and with the polarized continuum model (PCM) [36] in Gaussian 09. The solute is placed in a cavity constructed by superposition of van der Waals spheres around each atom. Point charges are placed on the surface of the cavity, which are brought to self-consistency for the interaction of the electron density of the solute and the solvent, represented as a dielectric continuum with its specific dielectric constant ϵ_r .

The dipole moment of charged molecules depends on the origin of the coordinate system. The fact that the optimal geometry of the complexes in their S_0 and T_1 states is different makes it difficult to define a unique origin for both states. Instead, we have fixed the origin to the center of mass for all species. Other choices lead to important changes in the values of μ , but hardly affect the difference between the dipoles of S_0 and T_1 ($\Delta\mu_{S_0-T_1}$).

A set of 60 different Ru(II) complexes has been screened. This set contains many complexes of the $[\text{Ru}(\text{L1})_2(\text{G}_2\text{L2})]^{2+}$ ($\text{L1} = \text{L2} = \text{bpy}$) type (Fig. 1), but also variants replacing either the L1 or L2 bipyridine ligand with 1,10-phenanthroline (phen), 1,4,5,8-tetraazaphenanthrene (tap), dipyrrodo[3,2-a:2',3'-c]phenazine (dppz), 2,2'-bipyrazine (bpz), or 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen). In addition to the substituents G considered in the probes synthesis, namely Cl (**1**), CN (**2**) and CH_3COO (**3**), the set contains 34 other groups. Figure 2 displays the structure of the most elaborated groups; others are depicted in the Supporting Information (Fig. S1). Firstly, we only calculated the dipole moments of the S_0 and T_1 states in their optimized geometry in the gas phase. Then we selected a subset of complexes mostly looking at the largest $\Delta\mu_{S_0-T_1}$, but also considering the complexity of their synthesis. For this set of 12 complexes, we calculated the Stokes shift in three different solvents of increasing polarity, namely, tetrahydrofuran ($\epsilon_r = 7.6$), ethanol ($\epsilon_r = 24.6$) and water ($\epsilon_r = 78.4$).

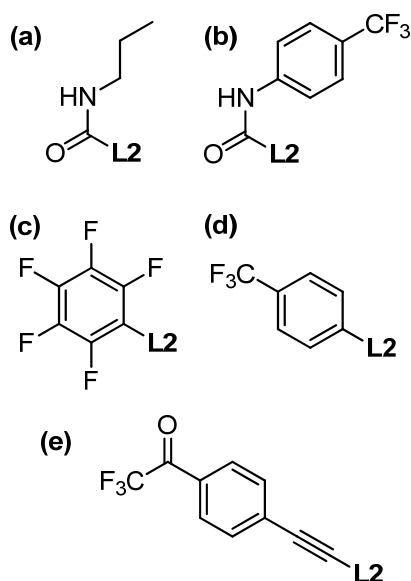


Figure 2. Structure of some of the groups that have been used in the computational study as substituents on the bipyridine ligand **L2** at the 4 and 4' positions. a) CONHC_3H_7 ; b) $\text{CONHC}_6\text{H}_4\text{CF}_3$; c) C_6F_5 ; d) $\text{C}_6\text{H}_4\text{CF}_3$; e) $\text{CCC}_6\text{H}_4\text{COCF}_3$.

3. Results and discussion

3.1 Computational results

Upon absorption of a UV or blue light photon, the $[\text{Ru}(\text{bpy}_3)]^{2+}$ dye is excited to a $^1\text{MLCT}$ state. Due to the large spin-orbit coupling of transition metal complexes, a very fast efficient intersystem crossing takes place, populating the $^3\text{MLCT}$ state. In this way, a metal $4d(t_{2g})$ electron is promoted to one of the three equivalent π^* orbitals of the coordinated bpy ligands.¹⁰ Coupling with the surrounding solvent dipoles induces localization of the electron on a single ligand.²⁸ In the case of coordination of the Ru(II) to three identical ligands, the $^3\text{MLCT}$ state becomes “randomized” by interligand hopping.²⁹ All these steps take place in a timescale of hundreds of femtoseconds. Finally, the dye relaxes from the $^3\text{MLCT}$ to the ground state by both non-radiative and radiative pathways. Consequently, the absorption and emission energies have been computed as the $S_0 \rightarrow S_1(^1\text{MLCT})$ and the $T_1(^3\text{MLCT}) \rightarrow S_0$ vertical transitions, at the minimum energy structures of the ground state and of the T_1 excited state, respectively.

3.1.1 Dipole moments of S_0 and T_1

The D_3 symmetry of the structure of the parent compound, $[\text{Ru}(\text{bpy})_3]^{2+}$, imposes a zero dipole moment in S_0 . The optimal geometry of the T_1 state is slightly distorted, leading to a MLCT state with an electron localized on one of the bpy ligands and a (calculated) moderate dipole moment of 4.97 D. In most of the substituted complexes, T_1 is of MLCT character, with the excited electron on either L1 or L2. However, in a few complexes, the lowest lying triplet state is characterized by a π - π^* excitation in one of the ligands (“intra-ligand” transition, or IL), without changing the number of electrons on the Ru core (Tables S1 to S3 in the Supporting Information). Electron-withdrawing substituents on the L2 ligand induce small dipole moments in the S_0 state and a T_1 state that is localized on the L2 ligand, whereas electron-donating groups tend to localize the excited electron on the L1 (non-substituted) ligands. In this way, the latter groups lead to a change of the sign in $\Delta\mu$. Surprisingly enough, the $\text{CCC}_6\text{H}_4\text{COCF}_3$ substituent (Figure 2) drives also the excited electron on the unsubstituted ligands (L1) and makes the dipole moment of the triplet state smaller than in S_0 ($\Delta\mu = -7.50$ D). Electron withdrawal through resonance leads to the largest changes in the dipole moment (for instance, we calculated $\Delta\mu$ to be 7.43 D for $\text{CONHC}_6\text{H}_4\text{CF}_3$) while the inductive effect through σ bonds is less pronounced. A list of the calculated dipole moments of all sixty compounds can be found in Tables S1 to S3 of the Supporting Information. Compounds are ordered by their electron-donating/electron-withdrawing and inductive/resonant character.

3.1.2 Selection of the final polarity indicator dyes

From the series of 60 complexes (Table S1), a representative selection of candidates was made, for which we calculated the Stokes shifts in three different solvents. Based on the largest dipole moment difference, synthetic accessibility and on the requirement that the S_1 and T_1 states have MLCT character, we have selected the $[\text{Ru}(\text{L1})_2(\text{G}_2\text{L2})]^{2+}$ complexes with $\text{L1} = \text{L2} = \text{bpy}$ and $\text{G} = \text{NO}_2$, CN , Cl , COOCH_3 , CF_3 , $\text{CONHC}_6\text{H}_4\text{CF}_3$, CONHC_3H_7 , C_6F_5 , $\text{SO}_2\text{NHC}_6\text{H}_4\text{CF}_3$, F and Br . Additionally, some other related complexes were considered for the sake of comparison: (i) the parent (i.e. unsubstituted) complex and its 3,4,7,8-tetramethylated derivative to add systems that undergo relatively small changes when going from S_0 to T_1 , and (ii) the $-\text{C}_6\text{H}_4\text{CF}_3$ substituent to compare the results with those of a $\text{Ru}(\text{II})$ complex whose CT excitation involves L2. The calculated absorption and emission energies and Stokes shifts for these dyes in solution are collected in Table 1 and Table 2; those Tables include bpy ligands

bearing substituents with mesomeric or inductive effects, respectively. A plot of the calculated Stokes shifts against the solvent polarity parameter Δf defined in eq. 2 shows a negative linear variation ($R^2 > 0.993$ in all cases). This slope is also listed in those Tables under the entry “L-M (Lippert-Mataga) slope” (eq. 1).

The first striking issue observed is that the L-M slope is negative for all complexes, in manifest contradiction to the Lippert-Mataga expression of eq. 1, which predicts a definite positive slope. The origin of this contradiction lies in the fact that the L-M model assumes that the absorbing and emitting states are of the same multiplicity and that the transitions involved do not entail electron transfer. A more detailed analysis of this issue will be provided below. Comparison of the L-M slopes in Table 1 and Table 2 shows that the substituents with mesomeric electronic effects provoke a larger variation of the Stokes shift with increasing solvent polarity, so that they are preferable to develop polarity probes based on Ru(II) complexes. Consequently, the next steps of our study focused mainly on this type of substituents.

In an actual luminescent sensor for polarity monitoring, the Ru complex must be embedded in a hydrophobic film [37]. This is usually carried out by attaching long alkyl (e.g. *n*-nonyl) or *tert*-butyl groups in the periphery of the indicator dye. Fortunately, the 4,4'-dinonylbipyridine ligand is commercially available to be used as the ancillary ligands (L1, see above). To model the effect of these chains on the L-M slope, two propyl substituents were additionally introduced in L1 of the complexes listed in Table 1, and the L-M slope was recalculated (Table S4, Supporting Information). Attaching the propyl group as model of the long aliphatic chains has a very small effect on the L-M slopes calculated for the unsubstituted analogues. There is a general tendency to slightly less negative slopes, except for the parent compound and the complexes with the CN and NO₂ substituents (see Table S4). This result indicates that the aliphatic chains are not significant for the electronic properties related to the Stokes shifts of the complexes.

Table 1

Calculated $S_0 \rightarrow S_1$ absorption energy, $T_1 \rightarrow S_0$ emission energy, Stokes shift, and Lippert-Mataga (L-M) slope (all in cm^{-1}) for $[\text{Ru}(\text{bpy})_2(\text{G}_2\text{bpy})]^{2+}$ complexes with mesomeric electron-donating or electron-withdrawing substituents (G) in water, ethanol and tetrahydrofuran (THF).

G	Solvent	$S_0 \rightarrow S_1$	$T_1 \rightarrow S_0$	Stokes Shift	L-M slope
$\text{C}_6\text{H}_4\text{CF}_3$	THF	20955	16047	4908	-1880
	EtOH	20750	16002	4748	
	H_2O	20684	15982	4702	
$\text{CONHC}_6\text{H}_4\text{CF}_3$	THF	19932	15229	4704	-1681
	EtOH	19786	15221	4564	
	H_2O	19738	15219	4518	
CONHC_3H_7	THF	20531	15768	4763	-1383
	EtOH	20255	15607	4647	
	H_2O	20166	15555	4611	
NO_2	THF	17235	13457	3778	-1299
	EtOH	16927	13255	3672	
	H_2O	16825	13192	3634	
CO_2CH_3	THF	19714	15360	4354	-1223
	EtOH	19458	15208	4250	
	H_2O	19339	15159	4220	
CN	THF	18375	14236	4139	-1192
	EtOH	18217	14177	4041	
	H_2O	18171	14164	4007	
C_6F_5	THF	20528	15800	4728	-1127
	EtOH	20372	15734	4638	
	H_2O	20327	15726	4602	
H	THF	21896	16614	5262	-976
	EtOH	21844	16658	5186	
	H_2O	21823	16677	5146	

Table 2

Calculated $S_0 \rightarrow S_1$ absorption energy, $T_1 \rightarrow S_0$ emission energy, Stokes shift, and Lippert-Mataga (L-M) slope (all in cm^{-1}) for $[\text{Ru}(\text{bpy})_2(\text{G}_2\text{bpy})]^{2+}$ complexes with inductive electron-donating or -withdrawing substituents in water, ethanol and tetrahydrofuran (THF).

G	Solvent	$S_0 \rightarrow S_1$	$T_1 \rightarrow S_0$	Stokes Shift	L-M slope
H	THF	21876	16617	5258	-976
	EtOH	21844	16658	5186	
	H ₂ O	21823	16676	5147	
Br	THF	20701	15566	5134	-935
	EtOH	20562	15507	5055	
	H ₂ O	20519	15487	5032	
Cl	THF	20822	15613	5209	-855
	EtOH	20705	15568	5137	
	H ₂ O	20669	15553	5116	
F	THF	21280	15805	5475	-806
	EtOH	21218	15810	5408	
	H ₂ O	21198	15812	5386	
CH ₃	THF	21555	16300	5200	-549
	EtOH	21466	16335	5132	
	H ₂ O	21454	16343	5111	
CF ₃	THF	19632	14755	4877	-536
	EtOH	19539	14712	4827	
	H ₂ O	19519	14700	4820	

3.2 Experimental results

If we focus on medium to highly polar solvents where the ionic Ru(II) polypyridyls are soluble enough, the absorption and emission spectra of complexes **1**, **2** and **3** generally shift hypsochromically with increasing polarity of the solvent (Figure 3). The maxima of the longest wavelength transition and of the emission band, together with the corresponding Stokes shifts, are collected in Table 3 for eight different solvents ordered by decreasing Lippert-Mataga polarity parameter (Δf). Actually, the variation of $\lambda_{\text{abs}}^{\text{max}}$ within this set (≤ 6 nm) is small compared to the observed variations of $\lambda_{\text{em}}^{\text{max}}$ (≤ 27 nm). This difference was expected from the much larger change in the dipole moment of the dye in going from the ligand-localized $^3\text{MLCT}$ to the ground state than from the latter to the delocalized $^1\text{MLCT}$ state (see above).

For the sake of completeness of the dyes characterization, the luminescence lifetimes and emission quantum yields of the dyes in various solvents have been measured and are collected in Table S5 and Table S6 (Supporting Information), respectively.

3.3 Comparison of the computational and experimental results

The first and most important comparison between experiment and computation concerns the L-M slope or, in other words, how sensitive the different substituted Ru(II) complexes are to changes in the polarity of the environment. Figure 4 collects the measured and calculated Stokes shifts of the complexes (**1**), (**2**) and (**3**), and Table 4 summarizes the numerical values of the L-M slopes. Although the calculated L-M slopes are smaller by a factor of four, but in all cases we found a negative slope and also the relative size of the experimental slopes is correctly reproduced. The computational strategy is a compromise between accuracy and efficiency; more sophisticated computational schemes can bring the absolute value of the slopes in closer agreement with the experimental data, but this would drastically reduce the efficiency of the screening procedure. The correct reproduction of the sign and relative magnitude of the slopes, validates the computational strategy followed in this study to select promising Ru(II)-polypyridyl candidates for polarity probes.

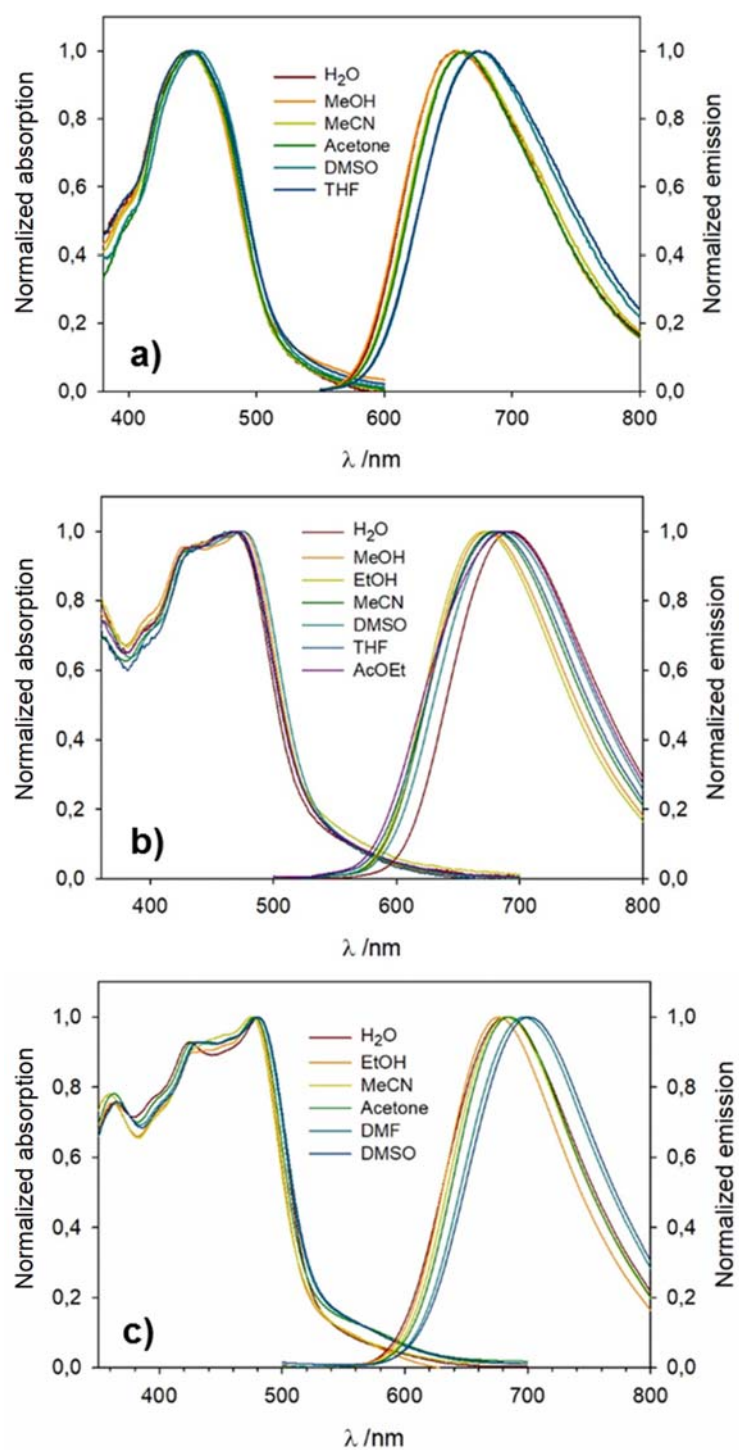


Figure 3. Normalized absorption and emission spectra of the probes (a) $[\text{Ru}(\text{bpy})_2(\text{Cl}_2\text{bpy})]^{2+}$ (**1**); (b) $[\text{Ru}(\text{bpy})_2(\text{CN})_2\text{bpy}]^{2+}$ (**2**), and (c) $[\text{Ru}(\text{bpy})_2(\text{CO}_2\text{CH}_3)_2\text{bpy}]^{2+}$ (**3**) in various solvents.

Table 3

Polarity parameter (Δf), maximum of the visible absorption and emission bands, and Stokes shift of Ru(II) complexes 1, 2 and 3 in different solvents.

Complex	Solvent	Δf^a	λ_{abs}^{max} /nm ^b	λ_{em}^{max} /nm	$\nu_{abs} - \nu_{em}$ /cm ⁻¹	L-M slope /cm ^{-1c}
1	H ₂ O	0.320	448	656	7078	-2900 ± 800
	Methanol	0.309	447	653	7057	
	Acetonitrile	0.305	449	662	7166	
	Ethanol	0.289	447	653	7057	
	Acetone	0.284	448	662	7216	
	Dimethyl sulfoxide	0.263	454	672	7145	
	Tetrahydrofuran	0.212	450	674	7385	
	Ethyl acetate	0.200	450	678	7473	
2	H ₂ O	0.320	472	695	6798	-3700 ± 400
	Methanol	0.309	469	674	6485	
	Acetonitrile	0.305	474	679	6370	
	Ethanol	0.289	470	671	6373	
	Acetone	0.284	469	671	6419	
	Dimethyl sulfoxide	0.263	475	686	6475	
	Tetrahydrofuran	0.212	467	681	6729	
	Ethyl acetate	0.200	471	689	6718	
3	H ₂ O	0.320	481	682	6127	-6900 ± 1300
	Methanol	0.309	474	677	6326	
	Acetonitrile	0.305	477	682	6302	
	Ethanol	0.289	474	676	6304	
	Acetone	0.284	477	684	6344	
	<i>N,N</i> -dimethylformamide	0.275	480	696	6466	
	Dimethyl sulfoxide	0.263	480	703	6609	
	Tetrahydrofuran	0.212	ns ^d	ns ^d	ns ^d	

^a Eq 2. ^b Longest wavelength MLCT transition. ^c Slope of the Lippert-Mataga plot, see eq. 1. ^d Not soluble enough.

Table 4

Comparison of the computed and experimental Lippert-Mataga slopes (in cm^{-1}) for the synthesized $[\text{Ru}(\text{bpy})_2(\text{G}_2\text{bpy})]^{2+}$ complexes.

Complex	Computed	Experimental
3 (G = CO_2CH_3)	-1223	-6900 ± 1300
2 (G = CN)	-1192	-3700 ± 400
(G = H)	-976	-3600 ± 1000
1 (G = Cl)	-855	-2900 ± 800

To analyse the different L-M slopes extracted from the experimental Stokes shifts and the calculated ones, we first consider how the absorption varies with the polarity of the solvent. The systematic study by Meyer and co-workers of the absorption energy of $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes versus the solvent polarity shows an increase of the transition energy as the polarity increases [38]. However, the changes are rather small, never exceeding 1 kcal/mol ($\sim 350 \text{ cm}^{-1}$). To the best of our knowledge there are no other recent experimental data for that compounds, and little has been published on the dependence of the absorption spectra on solvent polarity from the experimental point of view for other complexes. For example, for $[\text{Ru}(\text{dppz})(\text{phen})_2]^{2+}$ the influence on the emission spectra of the solvent has been extensively studied given to its particular luminescent behavior (it is not photoluminescent in water but does emit in nonaqueous solvents, see for example references [39] and [40]), while its absorption spectra does not show a significant influence by the nature of the solvent, showing that the MLCT absorption band is at slightly longer wavelengths in H_2O than in CH_3CN [39, 41]. Similar behavior is found for related compounds [42]

From the computational point of view, some works have been published on this issue. TD-DFT studies report absorption wavelengths for the MLCT band of $[\text{Ru}(\text{dppz})(\text{phen})_2]^{2+}$ in different solvents: in vacuum, acetonitrile and water the maxima of the absorption bands are located at 417, 445 and 449 nm respectively in reference [43] and at 423, 450 and 454 nm in reference [44]. These results are in partial agreement with the experimental data reported in [41], which show that the MLCT absorption band is observed at longer wavelengths in H_2O than in CH_3CN .

Less clear conclusions were extracted from the TD-DFT study of $[\text{Ru}(\text{bpy})_2(\text{bpy}-\text{E}-\text{Ph}-\text{E}-\text{Ipa})]^{2+}$ (E = ethynylene, Ph = *p*-phenylene, Ipa = isophthalic acid) [45]. Increasing polarity from benzene ($\epsilon =$

2.27) to ethanol ($\epsilon = 24.5$), the maximum absorption wavelength decreases, while it slightly increases from ethanol to acetonitrile ($\epsilon = 37.5$).

Regarding the fulfillment of the Lippert-Mataga equation, some authors have reported cases in which dyes display a behavior that is opposite to the predicted by this equation. For example, authors of references [37] and [45] describe a hypsochromic shift of the Ru(II) polypyridyls emission with increasing solvent polarity in a wide range, while changes in the absorption energy are reported to be small and no predominant trend has been established.

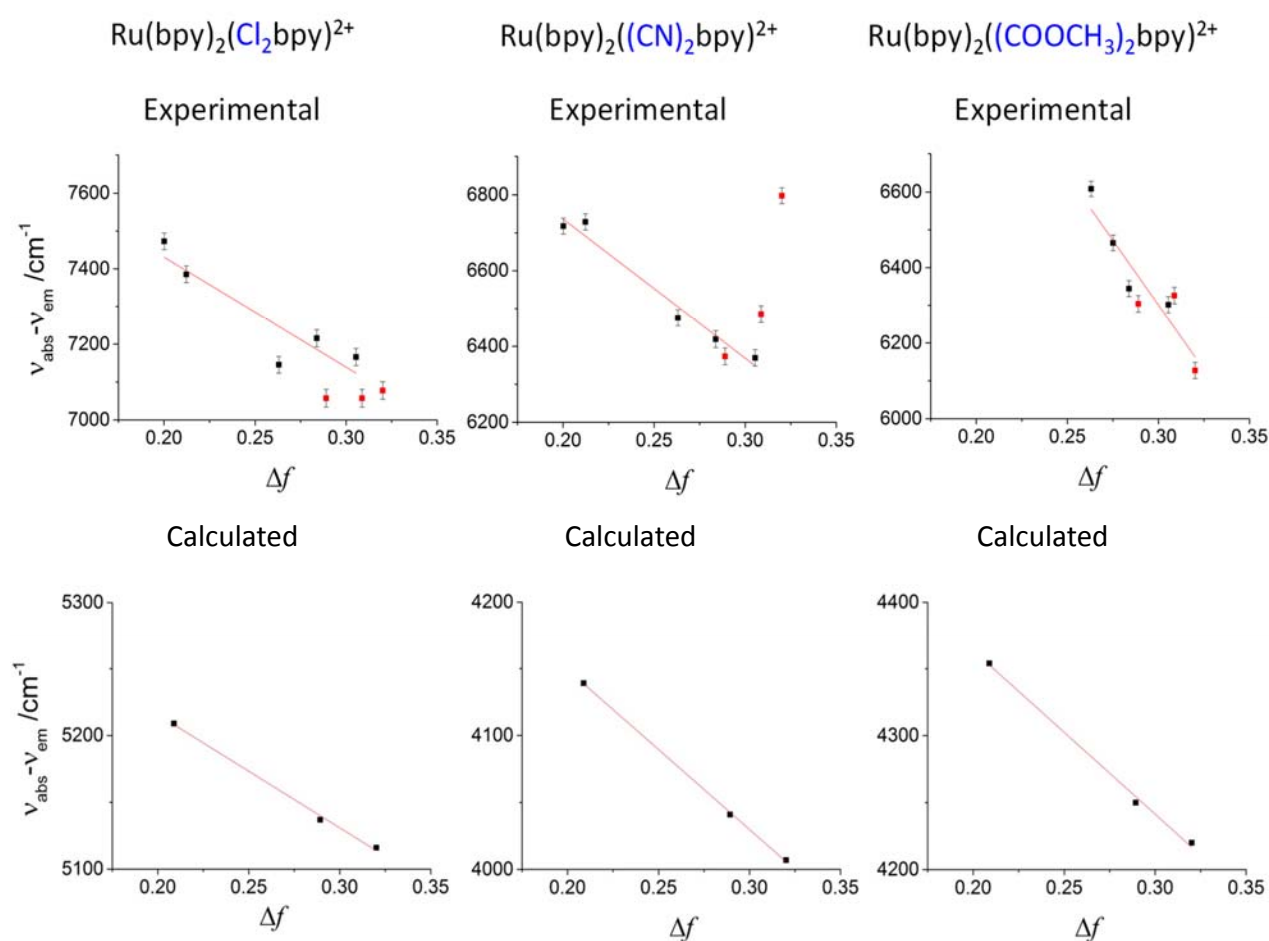


Figure 4. Experimental and calculated Lippert-Mataga plots for the heteroleptic Ru(II) dyes in Figure 1. The uncertainties in the experimental plots are the maximum estimated uncertainties derived from the choice of the maximum absorption and emission wavelengths. The data points in red correspond to the protogenic solvents (EtOH, MeOH and H₂O); they have not been included in the linear fits to determine the experimental L-M slope (see text).

Figure 5 shows the variation of the maximum absorption wavelengths with Δf for $[\text{Ru}(\text{bpy})_3]^{2+}$ and complexes (1), (2), and (3). Computational results are represented with grey dots while the experimental data are shown in blue or red color. The red dots correspond to the results obtained in the solvents that have also been modelled computationally. In all cases the theoretical absorption energy is lower than the experimental one. This is mostly due to the fact that we have taken the energy of the lowest S_1 state, which does not necessarily coincide with the maximum of the longest wavelength MLCT band, but rather to the onset of the band.

The computed absorption energies show a small yet steady increase with Δf , whereas the tendency in the experimental data is less clear. Some of the solvents undergo specific solvent-solute interactions that complicate the extraction of a general trend and are specifically excluded from the Lippert-Mataga treatment. These interactions are also missing in the computational modelling of the solvent. A detailed study with explicit solvent molecules might clarify the specific dependence of the absorption and emission energies on Δf , but it is beyond the scope of the present study.

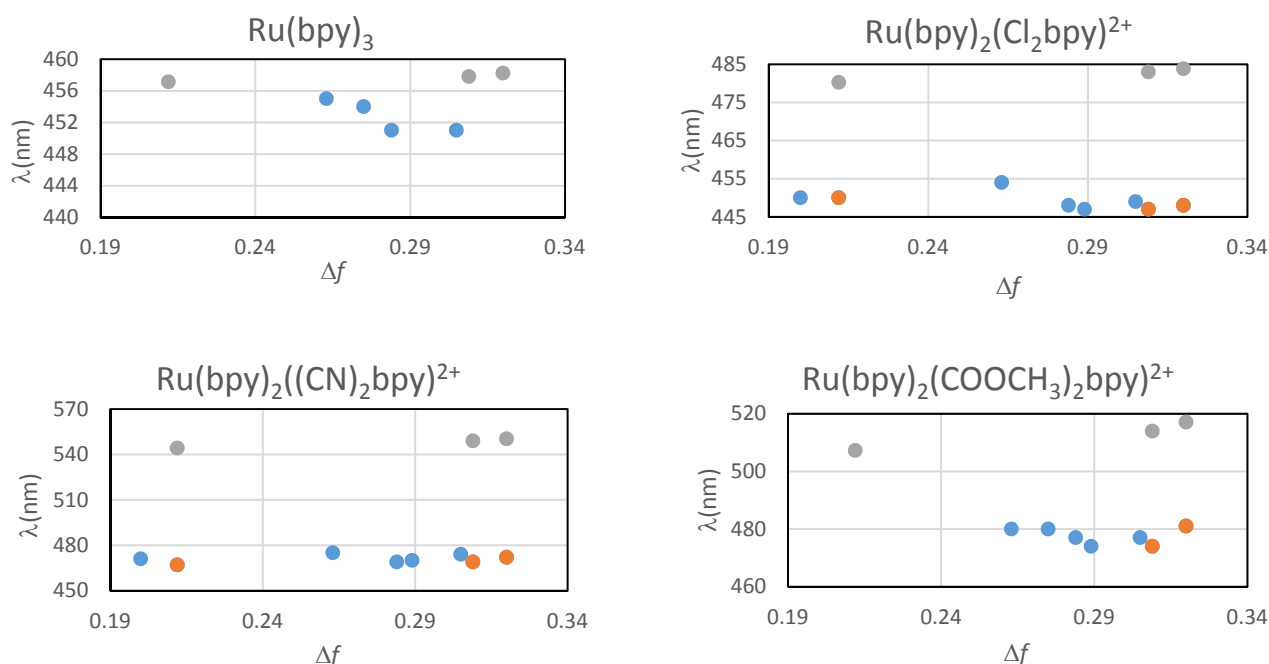


Figure 5. Absorption wavelengths (in nm) vs. the Lippert-Mataga parameter Δf . Experimental data are in blue or red color (the latter are those also subject to computational modelling) while computational data are in grey color.

3.4 Deviations from the Lippert-Mataga equation

In their analysis of the solvent effects on the absorption and emission energies, Lippert and Mataga placed the solute in a spherical cavity surrounded by a continuous polarizable medium. The dipole moments of the ground state (μ^G) and of the excited state (μ^E) were assumed to remain approximately constant when the solute relaxes to the optimal excited state geometry. Under this assumption, the fast component of the solvent stabilization (electronic rearrangement of the solvent molecules) does not contribute to the Stokes shift. Therefore, the latter exclusively depends on the slow component due to the reorientation of the solvent molecules around the solute. The resulting expression predicts a linear dependency of the Stokes shift on the solvent polarity Δf with a positive slope given by $(\mu_E - \mu_G)^2$ (see eq. 1 and Supporting Information for further details). In the Ru complexes studied here, we indeed observe a linear dependence of the Stokes shift on the solvent polarity, but the slope of the plot is negative, both computationally and in the experimental measurements.

Despite being a rather successful model, the L-M equation only covers part of the solvent-solute interactions. In addition to the aforementioned approximation of constant dipole moments, the L-M model does not consider intersystem crossing from the initially populated singlet excited state: the excited state populated by the photon absorption is also the state that originates the emission, the differences being only the orientation of the solvent molecules around the solute. To start with the latter approximation, this is obviously not the case for the Ru complexes studied here. The strong spin-orbit coupling promoted by the heavy metal core causes a rapid intersystem crossing from S_1 to T_1 and subsequent relaxation of the triplet state brings the system to the emitting ($^3\text{MLCT}$) species. The assumption of negligible changes in the dipole moment of ground and excited state upon the geometry relaxation does not seem to be justified, as the dipole moments of the S_0 , S_1 and T_1 states in the Franck-Condon region and at the relaxed geometry change significantly. Other effects such as hydrogen bonding cannot be used to explain the discrepancy between the L-M equation and the calculated results as they are not included in the computational approach. Such interactions are likely to be the reason for the underestimation of the calculated slopes compared to the experimental ones.

4. Conclusions

Heteroleptic Ru(II) polypyridyl complexes with electron-withdrawing substituents can be used as sensors of the microenvironmental polarity, yet they are less sensitive than elongated organic molecules that boast a lowest-lying intramolecular charge transfer (ICT) excited state with distant charge separation. Because of their phosphorescent emission, Ru(II) dyes do not behave as expected from the widely used Lippert-Mataga model. However, it is possible to predict their behaviour with changes in the solvent polarity by means of theoretical calculations. Such predictions will lead to better transition metal-based phosphorescent complexes to efficiently probe the polarity of sample gas or liquid mixtures (e.g. after immobilization of the sensor molecule in an adequate permeable polymer film), report on the polarity of biopolymers or cell structures to which they bind, and sense the micropolarity of materials using both the emission intensity and lifetime of their lowest-lying excited state.

Computational chemistry can help to point out which complexes are best suited to the task. Ideally, one would screen the metal complexes using the S_0 - T_1 dipole difference but, unfortunately, this approach does not contain enough information to discern those complexes with the largest changes in the Stokes shift when the polarity of the solvent is changed. Only by performing explicitly the calculation of the Stokes shift in different media, it is possible to select the best polarity-probing candidates.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/>

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