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Terthiophene Appended with Terpyridine Units as Receptors for Protons and Zn^{2+} Ions: Photoinduced Energy and Electron Transfer Processes

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Two ligands consisting of 2,2′:6′,2′′-terpyridine (tpy) and terthiophene units (3T) connected by a methyleneoxy (**TTT**) or an alkynyl bridge (**TAT**) show different photophysical properties: in the former there is no evidence of a ground state interaction between the two constituent chromophores and the expected 3T emission is observed. On the other hand, the latter exhibits strong π-conjugation between the two chromophores mediated by the alkynyl bridge: this results in a substantially redshifted absorption and an emission displaced toward the red with a decreased quantum yield. Both of these ligands can be diprotonated: protonation occurs at the tpy unit in two successive steps, leading finally to **TTT**·$2H^+$ and **TAT**·$2H^+$. In both cases, strong changes in the absorption spectra and very efficient quenching of the luminescence takes place by a photoinduced electron transfer from 3T to the protonated tpy unit. Both **TTT** and **TAT** can also perform as Zn^{2+} ligands, giving rise to complexes with 1:2 metal/ligand stoichiometry in acetonitrile solution, as demonstrated by changes in the photophysical properties. Also in this case, the resulting complex is not luminescent because of photoinduced electron transfer from 3T to the $[Zn(tpy)_2]^{2+}$ moieties.

Introduction

Oligothiophenes have received considerable attention as organic semiconductors with potential applications in field-effect transistors, lasing, nonlinear optics, light-emitting diodes, and solar cells.[1] Moreover, they are usually employed as starting materials for the synthesis of polythiophenes by electropolymerization or by chemical methods. Polythiophenes are organic semiconductors, which exhibit electrochromism, and electroluminescence: they have been widely investigated in the field of sensors, in particular as electrochemical sensors. A further step in this research topic consists of oligothiophene species appended with functional units able to modulate the physical and chemical properties of the resulting polymer, such as solubility, *p*-doping potential and band gap.[2] In particular, the presence of metal complexes along the polymer backbone is potentially interesting in terms of electrocatalysis, and the modulation of conductivity.[3]

2,2′:6′,2′′-Terpyridine (tpy) can be protonated and is known to be a good ligand for metal ions,[4] giving rise to highly luminescent Zn^{2+} complexes.[5] Moreover, the tridentate ligand offers several synthetic and structural advantages compared to bidentate ligands, such as bipyridine and phenanthroline. The resulting $[M(tpy)_2]^{2+}$ units provide a building block with defined topographical properties, very useful for the building of supramolecular structures according to a predetermined pattern.[4,6,7]

In this paper, we report two ligands consisting of a tpy and a terthiophene unit (3T) connected by a methyleneoxy (**TTT**, Scheme 1)[8] and an alkynyl bridge (**TAT**, Scheme 1).[9] The photophysical behavior of 3′-hydroxymethyl-2,2′:5′,2′′-terthiophene, hereafter called **TTOH**, has been reported as a model of the 3T unit. The use of terthiophene instead of simple thiophene as starting compound assures more accessible potential values for electropolymerization, high regioregularity and thus high conductivity of the resulting polymer. The value of the present systems relies on their ability to couple the properties of the terthiophene moiety, i.e. the possibility of electropolymerization to obtain a conducting polythiophene film, with that of the terpyridine units, performing as ligands of metal ions. We have recently reported the photophysical characterization of the corresponding Ru^{2+} complexes, showing an extraordinary long lifetime of the luminescent excited state of $[Ru(\mathbf{TAT})_2]^{2+}$ due to the strong conjugation of the 3T and tpy unit mediated by the alkynyl bridge.[10] In this paper, we have investigated the photophysical and electrochemical properties of **TTT**, **TAT**, and their protonated species, demonstrating efficient photoinduced energy and electron transfer processes. Strong luminescence changes take place upon

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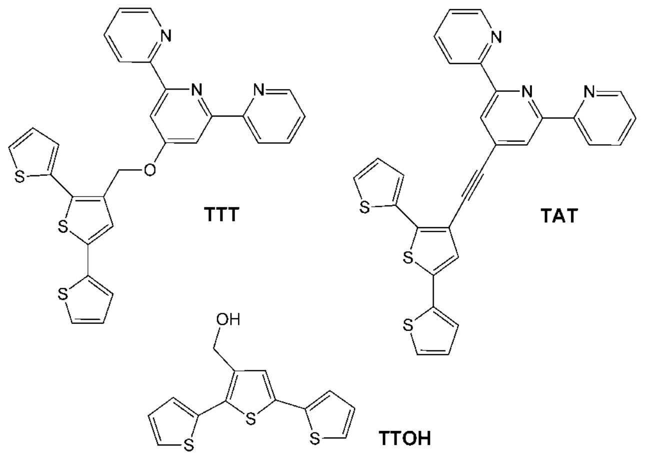
the complexation of Zn^{2+} ions by both ligands, demonstrating the formation of a complex with 1:2 metal/ligand stoichiometry. Therefore, these ligands can be used as sensors for protons and metal ions.



Scheme 1.

Results and Discussion

Photophysical Properties of the Ligands

As reported in Figure 1a, the absorption spectrum of **TTT** (green line) in acetonitrile solution is very close to the sum of those of the two component units, namely tpy (black line) and **TTOH** (blue line), so that the band at 280 nm is mainly due to the ππ* transition of the tpy unit,[5] and the lowest energy band at 343 nm is due to the ππ* transition of the terthiophene chromophore.[11] Upon excitation at 343 nm of an air-equilibrated **TTT** acetonitrile solution, the terthiophene emission with a maximum at 425 nm is observed, characterized by an emission quantum yield practically identical to that of **TTOH** (Table 1) and an excited state lifetime below the time resolution of our equipment (< 0.8 ns). The photophysical properties of **TTOH** and **TTT** are practically identical to those reported for α-terthiophene (λ_{em} = 415 nm, ϕ_{em} = 0.06, and τ = 0.17 ns in dichloromethane solution),[12] demonstrating that the methyleneoxy substituent does not affect the photophysical properties. Upon excitation of **TTT** at 280 nm, where most of the light is absorbed by the tpy chromophore, the same emission band is observed, while the very weak emission typical of the tpy unit is not registered. Quenching of the lowest singlet excited state (S_1) of tpy can take place by either energy transfer to the terthiophene or electron transfer from terthiophene to tpy (Scheme 2a). Indeed, based on the electrochemical data (see below, Table 2), the CT state lies at almost the same energy as the S_1 excited state of 3T. From the comparison of the excitation (λ_{em} = 425 nm) and the absorption spectra and the evaluation of the relative intensities of the 3T and tpy bands, an energy transfer efficiency of ca. 60% from tpy to 3T unit can be estimated. Therefore, both energy and electron transfer mechanisms are likely effective in quenching the S_1 excited state of tpy. On the other hand, no quenching of the 3T fluorescent ex-

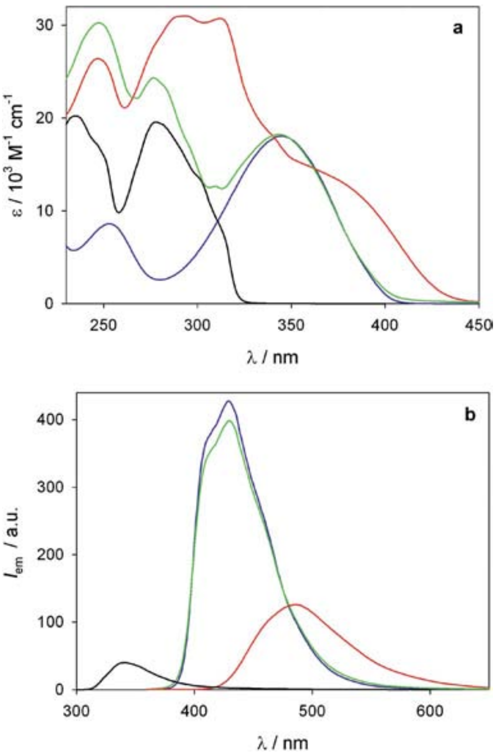


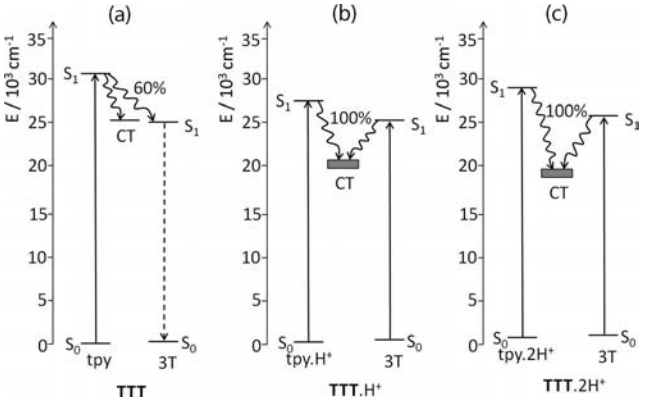
Figure 1. Absorption (a) and emission (b) spectra of **TTT** (green line), **TAT** (red line), **TTOH** (blue line), and tpy (black line) in acetonitrile solution at 298 K. Emission intensities are proportional to the corresponding emission quantum yield. Each emission spectrum was performed by exciting the lowest energy absorption band.

Table 1. Photophysical data for **TTT**, **TAT** compared to those of the model compounds **TTOH**, and tpy in air-equilibrated acetonitrile solution at 298 K and butyronitrile rigid matrix at 77 K.

	Absorption		Emission at 298 K			Emission at 77 K	
	λ_{max} [nm]	ε [10^4 M^{-1} cm^{-1}]	λ_{max} [nm]	ϕ_{em}	τ [ns]	λ_{max} [nm]	τ [ns]
TTOH	345	1.80	425	0.04	< 0.8	425	4.7
tpy[a]	277	1.95	338	0.003	–	–	–
TTT	345	1.82	425	0.04	< 0.8	425	3.5
TAT	312	3.01	485	0.02	< 0.8	485	4.3

[a] Data from ref.[5]

cited state is registered in a comparison with the model compound **TTOH**. In butyronitrile rigid matrix at 77 K, an emission band with the same maximum as that registered at 298 K is observed, confirming the $\pi\pi^*$ character of the corresponding transition,[13] while no phosphorescence is observed. The lifetime of the luminescent excited state is quite similar to that reported for **TTOH** (Table 1).



Scheme 2. Energy level diagram showing the relevant photophysical processes for **TTT** (a), **TTT**·H$^+$ (b), and **TTT**·2H$^+$ (c): absorption (solid lines), non-radiative deactivation (wavy lines), emission (dashed lines). CT is a charge transfer state corresponding to the electron transfer from the 3T to the tpy moiety: for (b) and (c) the corresponding energy is uncertain.

Table 2. Half-wave potentials ($E_{1/2}$) in V (vs. SCE), in acetonitrile/TEAPF$_6$ solution at 298 K, unless otherwise noted.

	$E_{1/2}$ [V] (vs. SCE)	
TTOH	+1.20[a]	
tpy[b]		–1.99
TTT	+1.12	–1.66[a]
TAT	+1.22[a]	–1.73[a]

[a] Chemically irreversible process; peak potential (E_p) at scan rate v = 0.5 V/s. [b] Data from ref.[19]

The absorption spectrum of **TAT** (Figure 1a, red line) does not overlap those of the component units and shows a considerable redshift of the lowest energy band compared to **TTOH**. Therefore, electronic ground state interactions take place, likely favoured by the alkynyl bridge, which allows a strong π-conjugation between the tpy and 3T units, contrary to that of the methylenoxy bridge of **TTT**.[14] The emission spectrum is redshifted (ca. 60 nm, Figure 1b) and is characterized by a lower quantum yield (Table 1) than **TTOH**. The excitation spectrum performed on **TAT**, with λ_{em} = 425 nm, closely matches the absorption spectrum, demonstrating that the stronger conjugation between tpy and 3T chromophores facilitates the photoinduced energy transfer from tpy to 3T unit, compared to **TTT**. In butyronitrile rigid matrix at 77 K, an emission band in the same position as that measured at 298 K is observed, and a lifetime of 4.3 ns is measured for the S$_1$ excited state of 3T, very close to that of **TTOH**.

Electrochemical Properties of the Ligands

The cyclic voltammograms of the two ligands,[8,9] performed in acetonitrile solution with tetraethylammonium hexafluorophosphate as the supporting electrolyte, exhibit a one-electron oxidation and a one-electron reduction process (Table 2), which are both chemically irreversible. In the case of **TTT**, the electron transfer process in the anodic region attains reversibility at scan rates higher than 5 V/s. On the basis of the model compound **TTOH** and tpy, we can assign the oxidation process to the 3T moiety and the reduction process to the tpy unit: the chemical irreversibility of the observed processes precludes the comparison of the thermodynamics of the electron transfer processes. The chemical irreversibility of the oxidation process is due to the well-known dimerization reaction of two terthiophene radical cations leading to a polymer[15] with formation of polymer films of **TTT**[8] and **TAT**[9] on the working electrode.

Protonation of the Ligands

Upon addition of CF$_3$SO$_3$H to a 4.2 × 10^{-5} M acetonitrile solution of **TTT**, large changes of the absorption spectra are observed with two distinct families of isosbestic points in the ranges 0–1 (Figure 2a) and 1–2 (Figure 2b) equiv. of acid per **TTT** molecule. Upon excitation at an isosbestic point (346 nm), strong quenching (> 95%) of the 3T emis-

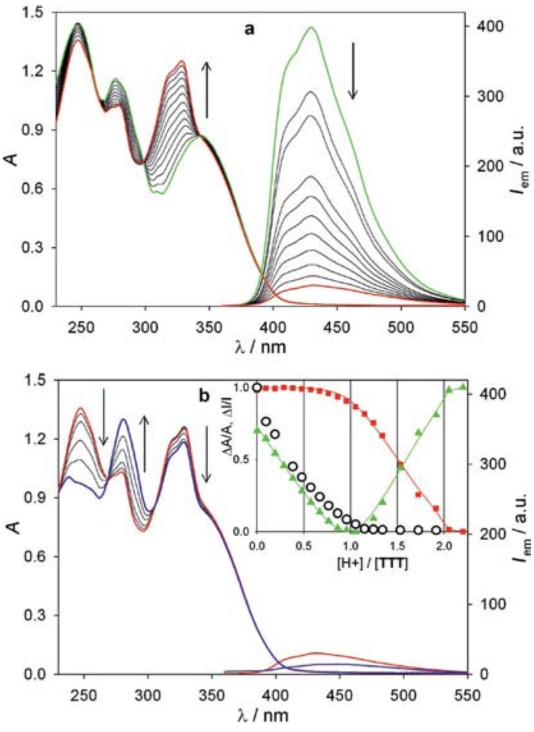


Figure 2. Absorption (left) and emission (right) spectral changes of a 4.7 × 10^{-5} M acetonitrile solution of **TTT** upon addition of 0–1 equiv. (a) and 1–2 equiv. (b) of CF$_3$SO$_3$H. λ_{ex} = 346 nm. Inset of (b) shows normalized absorption at 276 (green triangles), 247 nm (red squares), and emission intensity changes at 425 nm (empty circles) during the titration. Solid lines represent the fitting curves obtained by SPECFIT (see Experimental Section for details).

Table 3. Photophysical data for protonated forms of **TTT** and **TAT** as well as their Zn^{2+} complexes, compared to the corresponding forms of tpy in air-equilibrated acetonitrile solution at 298 K.

	Absorption		Emission at 298 K		
	λ_{max} [nm]	ε [10^4 M^{-1} cm^{-1}]	λ_{max} [nm]	ϕ_{em}	τ [ns]
tpy·H^{+}[a]	323	1.40	410	0.17	3.0
tpy·$2H^{+}$[a]	320	1.65	360	0.71	2.7
$[Zn(tpy)_2]^{2+}$[a]	330	1.54	353	0.65	–
TTT·H^{+}	345	1.82	425	0.002	< 0.8
TTT·$2H^{+}$	345	1.82	445	0.001	< 0.8
$[Zn(\textbf{TTT})_2]^{2+}$	345	1.82	430	< 0.001	–
TAT·H^{+}	319	2.99	485	0.003	< 0.8
TAT·$2H^{+}$	327	3.09	500	0.001	< 0.8
$[Zn(\textbf{TAT})_2]^{2+}$	420	0.67	500	< 0.001	–

[a] Data from ref.[5]

sion is observed by addition of ca. 1 equiv. of acid, with minor changes on successive acid addition. Normalized absorption plots reported in Figure 2b show that two successive protonation steps take place: the mono- (**TTT**·H^{+}) and diprotonated forms (**TTT**·$2H^{+}$) exhibit distinct absorption spectra, and both of them are characterized by a very weak luminescence (Table 3).

The basic site of **TTT** is the terpyridine unit, which is known to undergo two successive protonation processes either in aqueous[16] or acetonitrile solution:[5] both the protonated species of tpy are strongly luminescent (Table 3). The absorption spectra of **TTT**·H^{+} and **TTT**·$2H^{+}$ are consistent with the overlap between the absorption spectra of 3T and tpy·H^{+} or tpy·$2H^{+}$, respectively. Therefore, protonation of the terpyridine does not bring about significant changes to the terthiophene absorption. On the other hand, changes in the emission spectra show that the 3T emission is strongly quenched both in the mono- and diprotonated species, and no emission for both the mono- and diprotonated tpy units is observed. This behavior can be rationalized on the basis of the energy level diagrams reported in Scheme 2b and c. Upon protonation, reduction of the tpy unit becomes easier, so that the corresponding CT level is lower in energy than in the unprotonated **TTT**. The S_1 excited state of tpy·H^{+} and tpy·$2H^{+}$ as well as that of 3T lie at higher energy than the CT level, so that upon excitation of either the protonated terpyridine or the terthiophene moiety a photoinduced electron transfer from 3T to the protonated terpyridine units is likely to occur.

Global fitting of the absorption changes by SPECFIT (see Experimental Section for details) leads to the following values for the acidity constants: $pK_{a1} > 8$; $pK_{a2} = 6.4$.

In the case of **TAT**, large changes of both absorption and emission properties are observed upon addition of CF_3SO_3H (Figure 3). The absorption spectra show profound changes not only in the spectral region below 350 nm, dominated by the tpy absorption, but also in the lowest energy band corresponding to the 3T moiety with the appearance of a new broad band with a maximum at ca. 440 nm. This behavior demonstrates once more that in **TAT** the 3T and tpy moieties are strongly conjugated. Emission spectra show the disappearance of the band at 485 nm, upon excitation of an isosbestic point. Normalized absorption changes reach a plateau at ca. 2 equiv. of acid per **TAT** molecule, while the emission of 3T is strongly quenched upon addition of 1 equiv. (Figure 3, inset). As in the previous case, protonation involves the tpy unit, which can bind up to two protons. Protonation does not take place on a statistical basis since a clear discontinuity in the absorption plots can be observed at 1 equiv. of acid (solid symbols in Figure 3, inset). Moreover, monoprotonation of the tpy unit causes a strong quenching (> 95%) of the 3T fluorescence with a slight redshift of the residual emission. No emission is observed from the protonated terpyridine. The quenching of both the 3T and the protonated tpy emission for **TAT**·H^{+} and **TAT**·$2H^{+}$ can be attributed to a photoinduced electron transfer from 3T to the protonated tpy unit, as previously discussed for protonated **TTT** species.

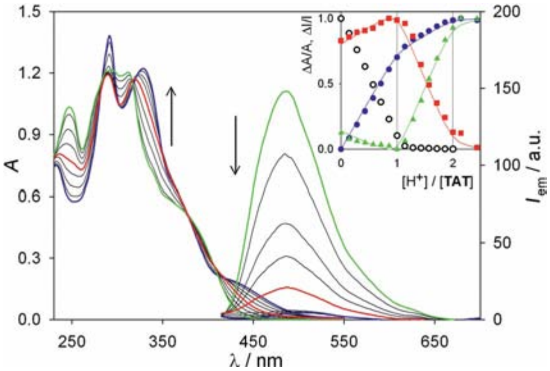


Figure 3. Absorption (left) and emission (right) spectral changes of a 4.2×10^{-5} M acetonitrile solution of **TAT** upon addition of CF_3SO_3H: 0 equiv. (green line), 1 equiv. (red line), 2.2 equiv. (blue line). λ_{ex} = 283 nm. Inset shows normalized absorption at 407 nm (red squares), 328 (blue circles), 291 (green triangles), and emission intensity changes at 486 nm (empty circles) during the titration. Solid lines represent the fitting curves obtained by SPECFIT (see Experimental Section for details).

Global fitting of the absorption changes by SPECFIT leads to the following values for the acidity constants: $pK_{a1} > 8$; $pK_{a2} = 6.2$, very similar to those previously reported for **TTT**. This result demonstrates that extended conjugation in the **TAT** ligand does not significantly affect the acid/base properties.

For both ligands, the reported spectral changes are completely reversible upon addition of a stoichiometric amount of triethylamine.

Zn^{2+} Complexation

The tpy ligand is known[5] to coordinate Zn^{2+} ions, forming complexes of 1:2 metal/ligand stoichiometry at low metal ion concentration: $[Zn(tpy)_2]^{2+}$ has a characteristic absorption spectrum clearly recognizable from the free ligand and is highly luminescent with a maximum at 353 nm in acetonitrile solution (Table 3).

Upon addition of $Zn(CF_3SO_3)_2$ to a 3.9×10^{-5} M acetonitrile solution of **TTT**, spectroscopic changes occurred similar to those observed upon protonation (Figure 4a). The absorption spectra show the appearance of a structured band at 320 nm, typical of $[Zn(tpy)_2]^{2+}$, and no change in the lowest energy band of the 3T moiety. With regard to the emission properties, the emission of 3T is strongly quenched and slightly redshifted, and no emission of $[Zn(tpy)_2]^{2+}$ is observed. From a quantitative point of view, both the absorption and emission changes reach a plateau at 0.5 equiv. of metal ion (Figure 4a, inset), which can be rationalized by the formation of the $[Zn(\mathbf{TTT})_2]^{2+}$ complex. Further addition of metal ion causes no change in the photophysical properties. Global fitting of the absorption spectral changes leads to a very high association constant for $[Zn(\mathbf{TTT})_2]^{2+}$, which cannot be measured by this technique: $\log\beta > 20$.

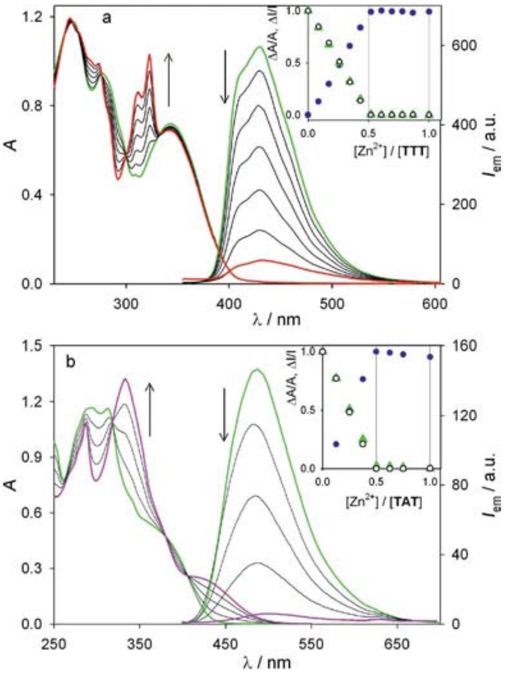


Figure 4. Absorption (left) and emission (right) spectral changes of a 4.2×10^{-5} M acetonitrile solution of **TTT** (a) and **TAT** (b) upon addition of $Zn(CF_3SO_3)_2$: 0 equiv. (green line), 0.5 equiv. (magenta line). λ_{ex} = 264 nm. Inset shows normalized absorption at 332 (blue circles), and 302 nm (green triangles), and emission intensity changes at the maximum (empty circles) during the titration.

In an analogy with the protonation behavior, the quenching of the 3T and $[Zn(tpy)_2]^{2+}$ emission can be attributed to a photoinduced electron transfer from 3T to the $[Zn(tpy)_2]^{2+}$ unit, which undergoes the first reduction at –1.40 V (vs. SCE),[17] at less negative potentials than the pure tpy, so that the corresponding CT state lies at 20300 cm^{-1} {< 28300 cm^{-1}, $[Zn(tpy)_2]^{2+}$ S_1 state}.[5]

In the case of **TAT**, similar results have been obtained upon titration with $Zn(CF_3SO_3)_2$ (Figure 4b). The absorption spectra show the appearance of the features of $[Zn(tpy)_2]^{2+}$, although slightly redshifted, and a new broad band at ca. 440 nm. The characteristic emission of $[Zn(tpy)_2]^{2+}$ is not observed, and that based on the 3T moiety is strongly quenched. This result can be rationalized in terms of a photoinduced electron transfer, as previously discussed for $[Zn(\mathbf{TTT})_2]^{2+}$. From a quantitative point of view, both the absorption and emission changes reach a plateau at 0.5 equiv. of metal ion (Figure 4b, inset). Global fitting of the absorption spectral changes leads to a very high association constant for $[Zn(\mathbf{TAT})_2]^{2+}$: $\log\beta > 20$.

Conclusions

Two ligands, consisting of terpyridine and terthiophene units and connected by a methyleneoxy (**TTT**) or an alkynyl bridge (**TAT**) show the luminescence of the 3T unit in acetonitrile solution, which is practically unaffected for the former, and shifted to the red and lower in intensity for the latter. These molecules can be protonated and are good ligands for the complexation of Zn^{2+} ions. Protonation occurs at the tpy unit in two successive steps, leading to $\mathbf{TTT}\cdot2H^+$ and $\mathbf{TAT}\cdot2H^+$: in both cases, strong changes in the absorption spectra and very efficient quenching of the luminescence takes place by a photoinduced electron transfer from the 3T to the protonated tpy unit. Formation of the $[Zn(\mathbf{TAT})_2]^{2+}$ complexes in acetonitrile solution have been observed by changes in the photophysical properties. Also in this case, quenching by photoinduced electron transfer takes place.

These systems are very attractive since they couple the properties of the terthiophene moiety, i.e. possibility of electropolymerization to obtain a conducting and electrochromic polythiophene film, with that of the terpyridine, which performs as a ligand for the complexation of metal ions. The observed quenching of the luminescence of **TTT** and **TAT** upon protonation or Zn^{2+} coordination can be exploited for the building of luminescent sensors with low detection limits (ca. 1 μM). However, the selectivity is not expected to be high with respect to transition metal ions since terpyridine is a good ligand for a variety of metal ions.[4] Future work will be aimed at studying the photophysical properties of an electrodeposited film of poly(**TTT**) and poly(**TAT**) on a transparent electrode and exploiting them as sensors of protons and metal ions. The presence of metal complexes along the polymer backbone is expected not only to change the luminescence properties, but also to modulate the film conductivity.

Experimental Section

Photophysics: The experiments were carried out in CH_3CN solution at 298 K and in butyronitrile rigid matrix at 77 K. UV/Vis absorption spectra were recorded with a Perkin–Elmer λ40 spectrophotometer. Fluorescence spectra were obtained with a Perkin–Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Fluorescence quantum yields were measured according to the method of Demas and Crosby[18] (standard used: anthracene in deaerated ethanol solution).[19] Luminescence spectra at 77 K were measured in a cylindrical tube immersed in a quartz Dewar vessel: the emission intensities registered under these experimental conditions suffer from low reproducibility, so no quantum yield is reported. Global fitting of absorption and emission spectra has been performed by SPECFIT software.[20] Fluorescence lifetime measurements were performed by an Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a D_2 lamp and an LDH-P-C-405 pulsed diode laser. The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient, fluorescence lifetime, steady-state fluorescence anisotropy at 298 K and $\log K$ values, 10% on the fluorescence quantum yield, and 15% on rotational correlation times, and steady-state fluorescence anisotropy at 77 K.

Electrochemistry: The electrochemical experiments were carried out in argon-purged CH_3CN solution at 298 K. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm^2), the counter electrode was a Pt spiral, and a silver wire was employed as a quasi-reference electrode (AgQRE). The potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene ($E_{1/2}$ = 0.39 V vs. SCE for Fc^+/Fc). The concentration of the compounds examined was of the order of 1×10^{-3} M; 0.1 M tetraethylammonium hexafluorophosphate ($TEAPF_6$) was added as supporting electrolyte. Cyclic voltammograms were obtained with scan rates in the range 0.05–20 V s^{-1}. The estimated experimental error on the $E_{1/2}$ value is ± 10 mV.

Acknowledgments

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