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Luminescent materials and devices: lanthanide azatriphenylene complexes and electroluminescent charge transfer systems

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Contents

Abstract

It is shown that the successful sensitization of lanthanide luminescence by azatriphenylenes can be expanded from sensitization in non-hydroxylic solvents to aqueous media by the

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addition of two or more carboxylate functionalities on the triphenylene skeleton. Furthermore, it is reported that a fluorescent donor–bridge–acceptor system incorporated in a thin polymer film allows the production of blue electroluminescence that can be tuned from blue to yellow by exposure to solvent vapours.

Keywords: Lanthanide luminescence; Energy transfer; Electron transfer; Antenna chromophores; Electroluminescence; Organic light emitting diode

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1. Introduction

Luminescent materials find an ever expanding number of applications ranging from those that involve extremely small amounts for detection purposes in (bio)molecular and forensic sciences down to the ultimate limit in single molecule spectroscopy and up to large-scale applications in macroscopic tagging, painting, illumination, and display technologies. Production of the luminescent excited state in these applications involves as widely different approaches as, for example, (multi)photon excitation, X-ray and e-beam excitation, and chemical as well as electrochemical reactions. In many cases the energy thus deposited in the luminescent material does not populate the luminescent state directly but rather leads to states that first undergo various internal conversion and relaxation processes. In our research group we focus our attention especially on intramolecular energy and electron transfer processes that lead to a luminescent state with particular desired properties. In the present paper we report recent progress made in designing energy transfer based lanthanide complexes and in solid state electron transfer based electroluminescence devices.

2. Luminescent lanthanide complexes

It has been recognized widely [1–7] that the usefulness of the long-lived and line-like emission of lanthanide ions goes far beyond its widespread application in solid state ‘phosphors’. Soluble molecular luminophores based on lanthanide emission may, for example, be employed as spectrally very discrete probes. Application of pulsed-excitation and time-gated detection furthermore allows their emission to be detected at very low levels even in (bio)media displaying strong but short lived autofluorescence.

The extremely weak absorption of lanthanide ions in the near UV–vis regions as well as the efficient quenching of their luminescence by energy loss to high frequency vibrational modes of the solvent, however, constitute major obstacles in the realization of such applications.

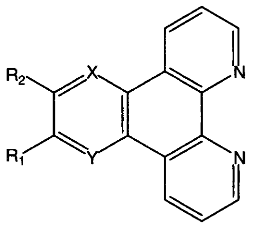
As shown in many earlier studies, these problems can in principle be overcome by coordination of the lanthanide ion to ligands that shield it from the solvent and that contain antenna chromophores capable to absorb near-UV–vis radiation and to transfer energy from their triplet state to the lanthanide [8,9].

2.1. Luminescent Eu(III) and Tb(III) complexes employing azatriphenylene-type antenna ligands

We reported recently [10,11] that di- and tetra-azatriphenylenes (see Fig. 1) constitute a very promising new class of antennae. This is especially so because the (aza)triphenylene π-system displays rather long wavelength absorption and features an exceptionally small energy gap between the lowest π–π* singlet and triplet states. The latter implies that following excitation in the near-UV efficient intersystem crossing to a high energy triplet state occurs. In fact the triplet energy of many (aza)triphenylenes is sufficiently high to allow fast and essentially irreversible energy transfer to most lanthanides [11]. Hereby e.g. not only the red luminescence of Eu(III) but also the green luminescence of Tb(III) can be sensitized with an oxygen insensitive and very high overall quantum yield (see Table 1) upon near UV excitation of the stable 2:1 complexes (see Fig. 1) that Ln(III) ions form with **1** and **2a–c** in acetonitrile.

While the antenna properties of azatriphenylenes are excellent and especially the fact that the same antenna can sensitize both Eu(III) and Tb(III) with around 50% efficiency (see Table 1) appears unprecedented, it should be noted that the stability of the complexes is relatively low. Especially hydroxylic solvents (including water) lead to complex dissociation and concomitant quenching of the luminescence.

As we proposed earlier [11], we have now started to extend several of our azatriphenylenes by the introduction of anionic ligand moieties to allow the formation of water stable and soluble complexes. While this project is still under active development, we here report some promising results already obtained.



	X	Y	R_1	R_2
1	CH	CH	H	H
2a	N	N	H	H
2b	N	N	H	Me
2c	N	N	$-(CH_2)_4-$	

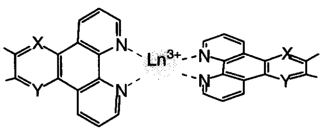


Fig. 1. Structure of some azatriphenylenes antennae investigated earlier and of the 2:1 antenna:lanthanide complexes they form in dry acetonitrile (see Table 1 for photophysical properties).

Table 1

Some photophysical properties of the antenna chromophores **1**, **2a–c** and the luminescence of their 2:1 antenna:lanthanide complexes (see Fig. 1) in dry acetonitrile as reported earlier [10,11]

Compound	$^1E_{00}$ cm^{-1} (nm)[a]	ε (M^{-1}·cm^{-1})	$^3E_{00}$ cm^{-1} (nm)[b]	τ_{Eu} (ms)	Φ_{Eu} (%)	τ_{Tb} (ms)	Φ_{Tb} (%)
1	29 700 (337)	1300	23 800 (420)	1.20 ± 0.02	41	1.31 ± 0.02	55
2a	29 400 (340)	3800	23 800 (420)	1.37 ± 0.02	41	1.67 ± 0.02	67
2b	29 400 (340)	8500	23 600 (424)	1.41 ± 0.02	43	1.41 ± 0.02	51
2c	28 820 (347)	6440	23 400 (428)	1.34 ± 0.03	37	1.37 ± 0.02	62

[a] In acetonitrile unless stated otherwise.

[b] From the 0–0 transition of the phosphorescence measured in EtOH:MeOH (4:1) glass at 77 K.

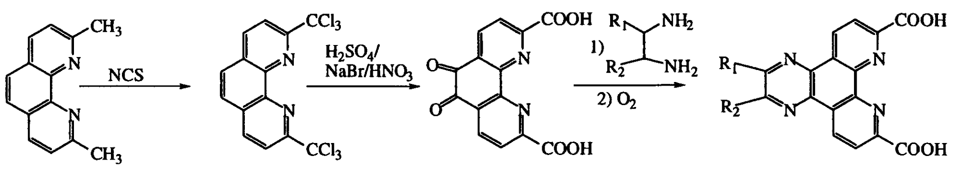
2.2. Water-stable lanthanide complexes based on tetra-azatriphenylene dicarboxylates

Following the synthetic route outlined in Fig. 2 the dicarboxylic acids **3a–c** were obtained [12] in ~ 75% overall yield.

The electronic absorption spectra (see Table 2) of **3a–c** are closely related to those of **2a–c** (see Table 1) although a slight red shift (ca. 5 nm) of the first absorption maximum is noted. This is of course advantageous with respect to the light-gathering power, but should not be accompanied by a reduction of the triplet energy that brings this near or even below the luminescent state of the lanthanide. The latter appears not to be a problem as evident from the fact that semiquantitative experiments revealed that **3a–c** sensitize the luminescence of both Eu(III) and Tb(III) and that in all cases the presence of oxygen has no significant effect on the luminescence intensity. As discussed extensively elsewhere [11] this implies that energy transfer from the triplet of the antenna to the lanthanides must be fast as well as irreversible (the latter on the time scale of the luminescence lifetime).

While the lanthanide complexes of **3a–c** thus share a relatively long wavelength excitability with those of **2a–c**, there are a number of significant differences. On the bright side it appears that the introduction of the two carboxylate ligands allows **3a–c** to bind lanthanide ions even in hydroxylic solvents including water (see also below). However, upon comparison of the data in Tables 1 and 2 it is evident that this transfer to hydroxylic solvents is accompanied by a significant drop in both lifetime and quantum yield of the luminescence. In view of the fact that both Φ and τ have diminished by about the same factor, it is evident that the main problem lies in an increase of non-radiative deactivation of the lanthanide excited state and not in a decrease of sensitization efficiency. This is most likely due to insufficient shielding of the lanthanide ion from the solvent as further supported by the titration curves discussed below.

Luminescence titration curves obtained with **3a–c** and Eu(III) (see e.g. Fig. 3) reveal a further complication with respect to an eventual application of these complexes as luminescent probes. Upon addition of the lanthanide to an aqueous solution of the antenna the lanthanide luminescence intensity increases until the stoichiometry of a 2:1 complex is reached. This behaviour is quite analogous to that



'Neocuproine'

3a $R_1 = R_2 = H$
3b $R_1 = H, R_2 = CH_3$
3c $R_1,R_2 = \text{-}(CH_2)_4\text{-}$

Fig. 2. Outline of the synthetic route leading to the tetra-azatriphenylene dicarboxylates **3a–c** employing ‘neocuproine’ as a common precursor.

Table 2
Some photophysical properties of the antennae chromophores **3a–c** and the luminescence of their 2:1 antenna:Eu(III) complexes in aqueous Tris–HCl buffer (pH 8.1)

Compound	${}^1E_{00}$ cm^{-1} (nm)	ε (M^{-1}·cm^{-1})	τ_{Eu} (ms)	Φ_{Eu} (%)
3a	29 070 (344)	2060	–	–
3b	28 820 (347)	4700	0.412	15 ± 5
3c	28 410 (352)	10500	0.306	17 ± 5

observed [10,11] for **1** and **2a–c** in acetonitrile solution. In the latter case the luminescence practically levels of at higher lanthanide/antenna ratios, indicating that the 2:1 complex is stable (or less likely that the quantum yield does not depend upon the complex stoichiometry). However, as evident from Fig. 3, the luminescence for **3b**/Eu3$^+$ in hydroxylic solution decreases significantly when more than 0.5 equivalents of lanthanide is added and only begins to level of at a significantly lower intensity beyond a 1:1 ratio. This phenomenon has been demonstrated earlier [13] for Eu(III) luminescence sensitized by related aza-aromatic dicarboxylates. It clearly indicates that the 2:1 and 1:1 complexes are of comparable stability, the latter having a significantly lower luminescence quantum yield, probably because of a higher solvent accessibility of the lanthanide ion in the 1:1 complex. This is further supported by luminescence lifetime measurements. Up to a 2:1 antenna/Ln^{3+} ratio a constant monoexponential decay time is found that we attribute to the 2:1 complex (see data in Table 2). However, at higher lanthanide concentrations the decay curves stay virtually monoexponential but the decay time decreases.

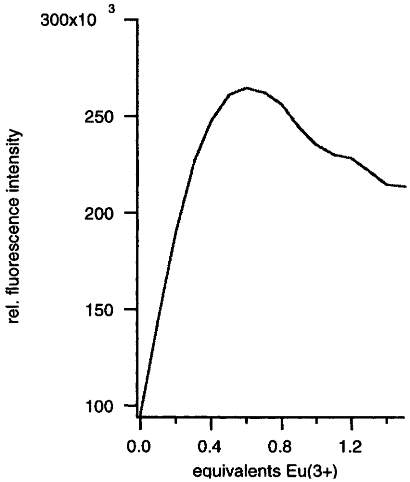


Fig. 3. Titration curve obtained by monitoring the Eu(III) luminescence (at 614 nm) resulting from excitation (at 350 nm) of an aqueous buffer (pH 8.1) solution containing ca. 10^{-5} M of **3b** and increasing concentrations of EuCl$_3$. The absorbance at the excitation wavelength remained virtually constant during the titration.

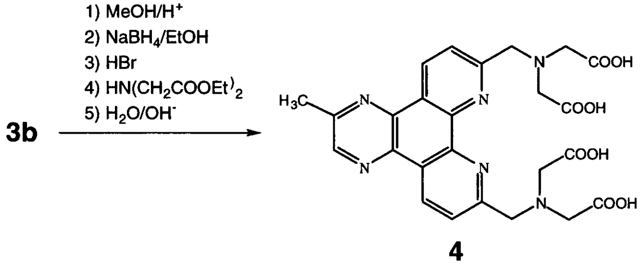
In conclusion antennae **3a–c** do allow sensitization of both Eu(III) and Tb(III) luminescence in hydroxylic solvents, but the quantum yields — although still respectable for lanthanides in aqueous solution — are considerably lower than obtained with similar antennae in non-hydroxylic solvent and furthermore the complex stoichiometry, and thereby the quantum yield, depends strongly on the relative concentrations of lanthanide and antenna.

2.3. Water-stable lanthanide complexes based upon a tetra-azatriphenylene tetracarboxylate

In order to enhance the complex stability, integrity and solvent exclusion properties we decided to follow an approach already established for other antenna chromophores structurally related to the azatriphenylenes in that they contain a phenanthroline moiety [13]. This approach essentially involves insertion of the bipyridyl part of the antenna in the central bond of EDTA. For this purpose **3b** was converted [12] into **4** via the steps outlined in Fig. 4 and essentially employing the conditions given by Coates et al. [13].

As expected from the properties of similar systems [4,14] **4** forms extremely stable complexes with lanthanide ions in aqueous solution, which have a 1:1 stoichiometry independent of the lanthanide and antenna ratio over a wide range of concentration. The latter is clearly related to the fact that at average pH one molecule of **4** can readily offer sufficient anionic sites to fully compensate the charge of a Ln^{3+} ion.

While, as anticipated, the structural modification from **3** to **4** enhances the stability and integrity of the 1:1 complex stoichiometry over a wide range of concentrations, the data collected in Table 3 show that this is not accompanied by an improvement of the luminescent properties as compared to the 2:1 complexes described in the preceding section. Again both the luminescence quantum yield and the luminescence lifetime are significantly below what has been achieved with **1** and **2** in non-hydroxylic media and for Eu(III) even slightly inferior to that of the 2:1 complexes of **3a–c** (see Table 2). Regarding the latter it must be noted, however, that the luminescent properties of the 1:1 Ln(III):**4** complexes appear superior to those of the 1:1 Ln(III):**3** complexes, which is in full accord with the observations



4

Fig. 4. Conversion of **3b** into the tetracarboxylate **4**.

Table 3
Luminescent properties of the 1:1 Eu(III):**4** and Tb(III):**4** complexes in aqueous buffer (pH 8.1) excitation at 337 nm

Lanthanide	τ (ms)	Φ^a (%)
Eu(III)	0.375	11
Tb(III)	0.388	15

[a] Estimated from the observed lifetime and assuming a radiative rate constant of 0.3 and 0.4 ms^{-1} for Eu(III) and Tb(III), respectively [11].

of Coates et al. [13]. Thus, although the solvent accessibility of the lantanide ion is reduced when one ligand of type **3** is substituted by **4**, a single type **4** ligand does not shield the lanthanide better (but in fact a little bit less) than two type **3** ligands. Furthermore, it cannot be excluded that the strong coordination sphere offered by **4** at the same time also offers one or more high frequency molecular vibrations that take over the role of the solvent OH oscillators as an energy drain. In this connection it should be realized that, for example, the NH groups and non-ionized COOH groups present in **4** can provide such an energy drain.

In conclusion, we have shown that it is possible to incorporate the azatriphenylene antenna motif in water-stable Eu(III) and Tb(III) complexes that can be excited in the near-UV and show lanthanide luminescence insensitive to quenching by oxygen. While the quantum yield of this luminescence is respectable (10–15%) it appears that in this respect there is ample room for improvement by further modification of the coordination sphere that the antenna offers to the lanthanide ion.

3. Electroluminescence from polymer embedded donor–bridge–acceptor systems

Electroluminescence of thin polymer films is the topic of many recent studies addressing its mechanism and its practical applications in so-called organic light emitting diodes (OLEDs) [15,16].

Regarding mechanistic aspects the electroluminescencent behaviour of polymer films constitutes an interesting borderline situation between that of bulk semiconductors and of molecular systems. In general terms, the electroluminescence results from the recombination of electrons and holes injected by electrodes attached to both faces of the film. Depending on the molecular structure of the film these holes and electrons may already have a strongly cation-radical- and anion-radical-like nature. Especially, however, the conversion of the energy resulting from charge recombination into photons seems quite analogous to that occurring during the recombination of molecular radical ions as, for example, studied extensively by Zachariasse [17] and as also known to occur in many electrochemiluminescent (ECL) processes in solution [18,19]. This mechanism implies that in most devices studied, the energy liberated upon charge recombination is converted into the excitation of a luminescent state, that is delocalized over a limited conjugation length in the polymer. Thus, in general, it is not the charge recombination process itself that is responsible for the luminescence observed and therefore the photon energy emitted is necessarily below the energy liberated in this charge recombination. We considered that it should be possible to increase the energy conversion efficiency of an OLED by making use of molecular systems in which intramolecular charge recombination itself is a radiative process. This is equivalent to what happens in electron donor–acceptor systems that display so-called charge transfer (CT) fluorescence from a state that can be considered as a radical ion pair constituted by the donor radical cation and the acceptor radical anion.

3.1. Blue electroluminescence from polymer embedded fluorotrope

From our studies on photoinduced electron transfer many donor–acceptor systems have in fact emerged, of which some have been found to display CT fluorescence with high quantum yields [20]. Such systems have now been found to be suitable for incorporation as the luminescent constituent in OLEDs with the added advantage that the position of their electrogenerated CT fluorescence can be tuned strongly (like that of their photoluminescence) by relatively minor changes of the matrix in which they are embedded. Here we report on the remarkable electroluminescent behaviour of the donor–bridge–acceptor system fluorotrope (FT) [21] in polyvinylcarbazole (PVK) and polystyrene (PS) (see Fig. 5). The name fluorotrope was chosen because of its strongly fluorescent nature and the presence of a tropane bridge that connects the *N*,*N*-dialkylaniline electron donor (D) and the vinylcyanonaphthalene electron acceptor (A) moieties.

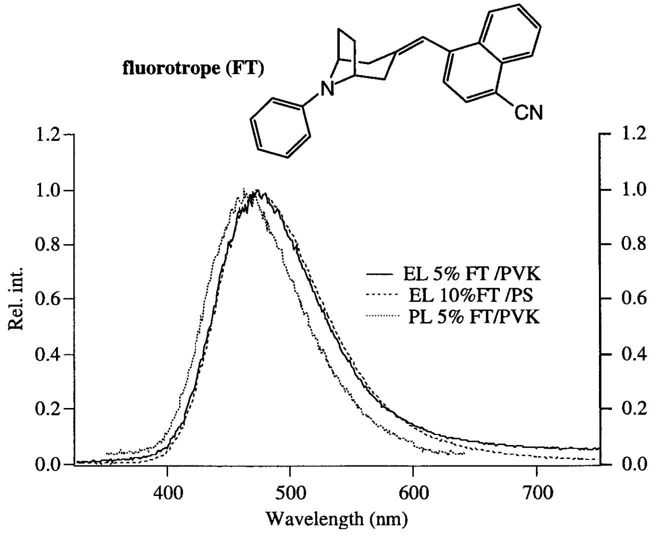


Fig. 5. Structure of FT, its photoluminescence (PL) in PVK and its electroluminescence (EL) spectra in PVK and in polystyrene.

Photoexcitation of either D or A in fluorotrope leads to extremely fast intramolecular electron transfer populating the CT excited state (D^+-bridge-A^-) that reverts to the ground state under the emission of CT fluorescence with high quantum yield. The emission maximum of this CT fluorescence occurs in the visible region and varies from the blue in non-polar alkane solvents (418 nm in cyclohexane) to the red in polar media (650 nm in acetone). The photoluminescence of systems like FT in polymer matrices has been studied extensively [22,23] and it has been found that also under these conditions they display strong CT fluorescence which changes its position dramatically as a function of the local polarity and mobility of the polymer matrix.

To test its electroluminescence capabilities FT (synthesis is described elsewhere [21]) and either poly(9-vinyl)carbazole (Aldrich, secondary standard) or polystyrene (BASF) were codissolved in a suitable solvent (1,4-dioxane for PVK and toluene for PS). A thin film containing 1–10% by weight of FT in the polymer was applied by spincoating from a 10 mg ml^{-1} solution on a glass slide coated with indiumtinoxide (Balzers). The obtained films are typically of 100 nm thickness. On top of the polymer film aluminium electrodes were vacuum deposited. The photoluminescence of the polymer films was measured employing front-face excitation in a SPEX Fluorolog 3 spectrofluorometer. The spectral distribution of the electroluminescence was measured employing a fibre coupled spectrograph (Acton SP150) to disperse the light on a Peltier cooled Princeton Instruments CCD detector.

The photoluminescence (see Table 4) of pure and FT-doped polymer films were measured employing front-face excitation at 320 nm. Under these conditions PS displays no fluorescence because its absorption is negligible above 300 nm, while PVK displays the well known mixed monomer and excimer fluorescence as a broad structureless band with a maximum at 410 nm. In PS, the CT emission maximum of FT is 467 nm at a concentration of 10% by weight. The fluorescence of FT in PVK was studied as a function of the FT concentration. Already at 1% FT in PVK

Table 4
Photoluminescence (PL) and electroluminescence (EL) emission maxima of various concentrations of FT in PVK and PS

	λ_{max} PL (nm)	λ_{max} EL (nm)
Polymer PVK		
0%	410	[a]
1%	460	–
2%	463	475
5%	465	475
10%	475	490
Polymer PS		
0%	–	–
5%	455	–
10%	467	475

[a] Some PVK-lots displayed a weak (impurity induced) electroluminescence at 620 nm.

the 410 nm emission of PVK is substituted by the longer wavelength emission of FT that undergoes a moderate bathochromic shift with increasing concentration from 460 nm at 1% to 475 nm at 10%. The position and spectral distribution of this emission remains unchanged when the excitation wavelength is shifted from 320 nm, where most absorption occurs by PVK, to 380 nm, where only FT absorbs. It can therefore be concluded that efficient energy transfer from PVK to FT occurs. The concentration dependence of the CT fluorescence maximum indicates that especially at higher concentrations a certain degree of aggregation of the fluorotrope molecules in the matrices occurs.

To study electroluminescence a regulated voltage supply with current limitation was connected to the ITO (positive) and aluminium (negative) electrodes and the voltage was raised until electroluminescence appeared. Typical electroluminescence spectra obtained for an OLED containing 5% of FT in PVK and 10% of FT in PS are shown in Fig. 5 as well as the photoluminescence from a thin film.

The spectral distribution of the electroluminescence is voltage independent between the turn-on voltage of ca. 14 V to breakdown at ca. 45 V, and slightly red-shifted compared to that of the photoluminescence. Above 22 V the light output increases almost linearly with the voltage (see Fig. 6).

In Table 4 the position of the emission maxima of both the photoluminescence and the electroluminescence are given for the various film compositions investigated. It is well known that the limited stability of OLEDs due to, for example, oxidative breakdown is one of the major bottlenecks for their practical application. The present systems, in which no special stability enhancing measures have been taken, are no exception to this rule. The light production typically reduces to half during the first minutes, after which the light production diminishes much more slowly over about an hour. If the same 'unsophisticated' OLED is operated in a more inert atmosphere this easily increases to over 2 h.

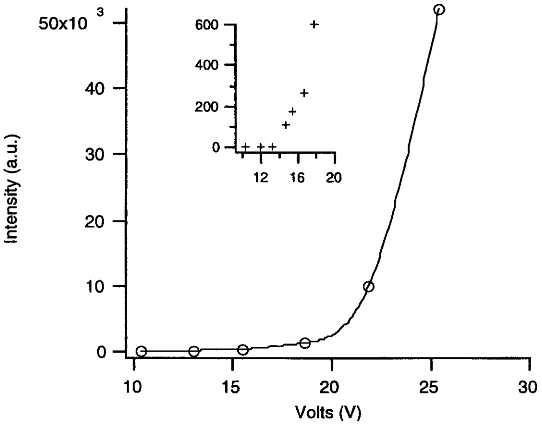


Fig. 6. Light intensity vs. voltage of a 5% FT/PVK light-emitting diode; the inset shows a magnification of the turn-on voltage region.

3.2. Blue to yellow vapochromic tuning of electroluminescence

As shown above the electroluminescence wavelength of fluorotrope can be changed to a certain extent by variation of the embedding polymer and of the doping level. High sensitivity of the fluorescence wavelength for changes in the surrounding medium is typical for emission from an excited state with a large dipole moment (which is thus strongly stabilized in a polar environment) to a ground state with a much smaller dipole moment. As already mentioned in the previous section, fluorotrope and related systems are known to display an extreme form of such medium sensitivity. This is because charge separation in the ground state is negligible while in the lowest excited state complete electron transfer from the aniline type donor chromophore to the vinylcyanonaphthalene electron acceptor moiety takes place which increases the dipole moment of the excited state by more than 25 Debye as compared to that of the ground state. In solution this makes that the charge transfer (CT) fluorescence of fluorotrope shifts from blue in non-polar media (418 nm in cyclohexane) to red in polar media (650 nm in acetone). It is known from earlier investigations [23,24] on the photoluminescence of fluorotrope and related systems that after embedding these in polymer latex particles or in thin polymer films the fluorescence wavelength can still be shifted strongly by contacting the polymer matrix with solvents (or their vapour) that penetrate the polymer network and can thereby reach the embedded fluorotrope molecules. This was now found to enable an enormous tuning of the electroluminescent wavelength of the fluorotrope based OLEDs also. As a dramatic example we show in Fig. 7 the tuning of a PVK/FT OLED from blue (480 nm) to yellow (650 nm) upon exposure to the vapour of an organic solvent (i.e. dichloromethane) which rapidly penetrates the thin polymer film.

While, as discussed above, the shift of the fluorescence of systems like FT in a polymer matrix by ‘swelling’ with various low molecular weight solvents or vapours has been described extensively [23,24] it is applied here for the first time to tune the

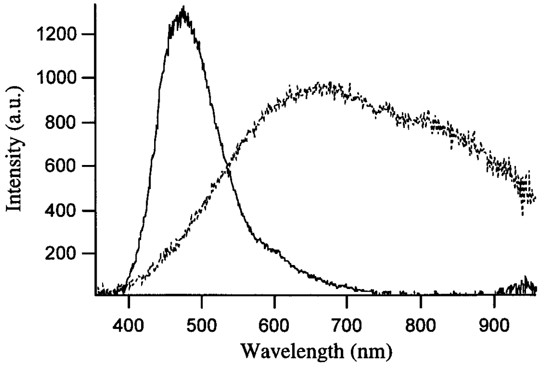


Fig. 7. Electroluminescence spectra of a 5% FT/PVK light-emitting diode before (continuous line) and after (dashed line) exposure to dichloromethane vapour.

wavelength of an OLED over a range unprecedented for 'vapochromic' tuning [25] of such a device.

In conclusion, electrogeneration of the intramolecular CT fluorescence of the donor–bridge–acceptor system FT occurs readily in polymer films. This is not only the case in a hole-conducting polymer like PVK but even in a strongly insulating polymer like PS. Especially in the latter case it appears that hole injection (i.e. oxidation of the donor moiety, step (1)) and electron injection (i.e. reduction of the acceptor moiety, step (2)) occurs directly in molecules of FT residing close to the anode and the cathode, respectively. Degenerate charge hopping between neighbouring molecules then occurs until a 'hole' and 'electron' reside on the same molecule (step (3A)), which is equivalent to formation of the CT excited state, that finally relaxes by intramolecular charge recombination under the emission of CT fluorescence, $h\nu_{\mathrm{CT}}$ (step (4)). In PS, such charge hopping requires that a closed pathway of molecules FT exists between the electrodes. This percolation limit condition is apparently fulfilled for 10% FT in PS but not for 5% and lower. In PVK lower concentrations of FT can be used, probably because here the polymer can act as a hole transport medium. Ultimately the positive charge will be trapped on FT because the oxidation potential of *N*-methylcarbazole is around 1 V [26] as compared to 0.7 V for FT (in acetonitrile vs. SCE).

Clearly the formation of the CT excited state in step (3A) is most crucial since it has to compete with the 'dark' intermolecular charge recombination (step (3B)).

$$\text{D-bridge-A} - e^- \rightarrow \text{D}^+\text{-bridge-A} \tag{1}$$

$$\text{D-bridge-A} + e^- \rightarrow \text{D-bridge-A}^- \tag{2}$$

$$\text{D}^+\text{-bridge-A} + \text{D-bridge-A}^- \rightarrow \text{D-bridge-A} + \text{D}^+\text{-bridge-A}^- \tag{3A}$$

$$\text{D}^+\text{-bridge-A} + \text{D-bridge-A}^- \rightarrow 2(\text{D-bridge-A}) + \text{heat} \tag{3B}$$

$$\text{D}^+\text{-bridge-A}^- \rightarrow \text{D-bridge-A} + h\nu_{\mathrm{CT}} \tag{4}$$

It should be noted that the electron transfer process (step (3B)) is much more exergonic than step (3A), the difference being the energy of the CT excited state, which is in the order of 2.7–2.1 eV as judged by the energy of the CT emission maximum. This implies that step (3B) occurs far in the Marcus inverted region [27,28]which may slow it down sufficiently to make step (3A) the favoured mode of electron exchange when 'hole' and 'electron' meet. That the energy of charge recombination can be deposited largely in the relatively high energy CT excited state of FT, and the fact that the CT state itself is the emitter without the need for further energy wastage to populate a lower energy emissive state of localized nature, is probably the reason why blue emission can readily be produced in these simple OLEDs. Stabilization of the CT excited state by microsolvation furthermore provides a straightforward method to tune the emission towards the red.

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