Sensitized near-IR luminescence of lanthanide complexes based on push-pull diketone derivatives†

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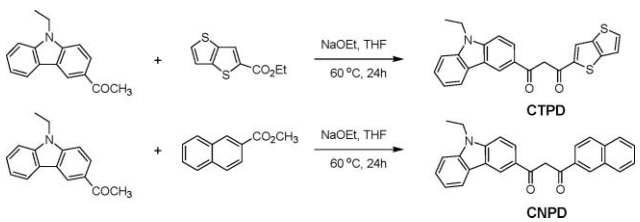
Lanthanide complexes with two push-pull diketone derivatives as sensitizers have been developed as synthons for near-infrared emitting materials. The ligand substituents consist of a carbazole moiety with hole-transport properties and an aromatic or heteroaromatic unit. According to quantitative NMR analysis and complementary HPLC experiments, the diketones are predominantly in their enolic form in polar solvents such as THF and MeCN at room temperature. The preferred *cis*-enol form contributes strongly to the binding of lanthanide ions (Ln = Nd, Gd, Er). The resulting tris(diketonate) ternary complexes with terpyridine (Ln = Nd, Er) display sizeable near-IR emission with long luminescence lifetimes.

Introduction

Highly luminescent lanthanide complexes are attracting attention in a wide variety of photonic applications such as planar waveguide amplifiers,[1,2] light-emitting diodes[3] and bio-inspired luminescent probes.[4] The design of organic photosensitisers has dominated the development of smart lanthanide-based optical devices in view of their high molar absorption coefficients, flexibility of molecular design, as well as their efficient sensitization ability of the metal-centred luminescence. In particular, this approach allows the enhancement of the emission intensity and quantum yield of near-infrared (NIR) emitting lanthanide ions.[5] Among the numerous ligands tested to date, β-diketonates[6] appear to be adequate sensitizers for tailoring luminescent lanthanide complexes in which either visible or NIR emission is consecutive with photo-induced energy transfer from the sensitizing ligand.[7] In order to use lanthanide tris(β-diketonates) as emissive layers in electroluminescent devices, "push-pull" ligands have been synthesized which feature a carbazole substituent as electron donor and a naphthalene or fused thiophene group as electron acceptor. Additionally, the coordination sphere of the lanthanide ion is usually completed by the use of an ancillary ligand such as 2,2′:6′,2″-terpyridine (tpy).[8,9] Although β-diketonates provide strong bidentate binding sites for lanthanide ions, they commonly exist as keto-enol tautomers, a proportion of which is intrinsically affected by the β-diketone substituents.[10,11] Furthermore, the characteristic electronic states of the ligands is significantly influenced by the solvent polarity.[12]

In this work, we investigate further these phenomena by presenting the synthesis of two push-pull diketone derivatives, CTPD and CTNP (see Scheme 1) and by determining their keto-enol ratio by ^{1}H-NMR and HPLC analysis, as well as their solvatochromic behaviour. Furthermore, ternary tris(β-diketonate) complexes with tpy are isolated and the photophysical properties of the Nd(III) and Er(III) complexes are investigated on a quantitative basis.



Scheme 1 Synthesis of β-diketone ligands.

Experimental

Materials and methods

NMR spectra were measured at 25 °C on Bruker Biospin with CryoProbe™ (1D, ^{1}H, 800 MHz) and Bruker Avance DRX 400 (2D-COSY experiments, ^{1}H, 400 MHz) spectrometers. Spectra were recorded in CD_3CN (99.8%, Aldrich) or THF-d_8 (99.5%, Armar chemicals); deuterated solvents were used as internal standards and chemical shifts are given with respect to TMS. Methyl 2-naphthoate was obtained from TCl Co. and used without further purification. 3-Acetyl-9-ethylcarbazole[13] and ethylthieno[3,2,-*b*]thiophene-2-carboxylate were synthesized according to literature methods.[14] HPLC experiments were performed on a Waters 600 apparatus (pump and controller) with a Waters 2487 dual λ absorbance detector using a reverse phase column (Waters Symmetry C_{18}, 3.5 µm, 4.6× 75 mm) with an acetonitrile–water eluent starting from 0% acetonitrile and increasing by 1% per minute.

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Photophysical data

Luminescence spectra of the ligands and quantum yields of the complexes were measured on a Fluorolog FL-3-22 spectrometer from Horiba-Jobin-Yvon Ltd.; quartz cells with optical paths of 0.2 cm were used for rt spectra while low-temperature measurements were carried out on samples in quartz Suprasil® capillaries. Detectors were a Hamamatsu R927 photomultiplier for the visible range and a cooled InGaAs detector from Electro-Optical Systems Inc. (DSS-16A02OL) for NIR measurements. Emission spectra were corrected for the instrumental function regularly updated. Quantum yields were determined on solid samples at 295 K, under ligand excitation, according to an absolute method using a home-modified integration sphere.[15] Each sample was measured several times under slightly different experimental conditions. The estimated error for quantum yields is 10–20%. Luminescent lifetimes were determined upon excitation at 355 nm provided by a Quantum Brillant Nd:YAG laser equipped with a frequency tripler; the emitted NIR light was analysed at 90° on a home-built setup comprising a Spex 1870 single monochromator with 950 grooves/mm holographic gratings blazed at 900 nm. Light intensity was measured with a Hamamatsu H9170-75 photomultiplier cooled by the Pelletier effect at −60 °C and coupled to a Stanford Research SR430 multichannel scaler. Lifetimes are averages of three independent determinations.

Preparation of 3-acetyl-9-ethylcarbazole[13]. Yield 58%, mp = 116–117 °C; ^{1}H-NMR (300 MHz in $CDCl_3$-d_1): δ = 8.76 (s, 1H, Ar–H), 8.2 (t, 2H, Ar–H), 7.53 (s, 1H, Ar–H), 7.40–7.47 (m, 2H, Ar–H), 7.31 (t, 1H, Ar–H), 4.38 (q, 2H, -CH_2CH$_3$), 2.74 (s, 3H, -COCH$_3$), 1.43 (t, 3H, -CH$_2$CH_3); Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90, Found: C, 80.61; H, 6.43; N, 6.27.

Preparation of the CTPD ligand. 3-Acetyl-9-ethylcarbazole (1.10 g, 4.64 mmol) and ethyl thieno[3,2,-*b*]thiophene-2-carboxylate (1.18 g, 5.56 mmol) were dissolved in 25 mL anhydrous THF under a N_2 atmosphere. Sodium ethoxide (0.38 g, 5.56 mmol) was added. After stirring for 24 h at 60 °C, hydrochloric acid (1.0 M) was added to the solution. The crude mixture was extracted with CH_2Cl_2 and dried over anhydrous magnesium sulfate. The residue was purified by column chromatography (ethyl acetate : hexane = 1 : 3) to give the final product as a yellowish solid. Yield 65%, mp = 135 °C; EI-MS Calcd for $C_{23}H_{17}NO_2S_2$ 403.07, Found [M$^+$] 403; Anal. Calcd for $C_{23}H_{17}NO_2S_2$: C, 68.46; H, 4.25; N, 3.47; S, 15.89. Found C, 68.75; H, 4.45; N, 3.45; S, 16.02.

Enol form: (2*Z*)-1-(9-ethyl-9*H*-carbazol-2-yl)-3-hydroxy-3-thieno[3,2-*b*]thiophen-2-ylprop-2-en-1-one. ^{1}H-NMR (800 MHz in THF-d_8): δ = 8.90 (s, 1H, H^1); 8.30 (s, 1H, H^{enol}); 8.22 (d, 1H, ^3J = 7.58 Hz, H^8); 8.18 (d, 1H, ^3J = 7.58 Hz, H^5); 7.75 (d, 1H, ^3J = 5.13 Hz, H$^{5'}$); 7.61 (d, 1H, ^3J = 8.56 Hz, H^{3,4}); 7.56 (d, 1H, ^3J = 8.56 Hz, H^{3,4}); 7.49 (t, 1H, ^3J = 7.58 Hz, H^6); 7.42 (d, 1H, ^3J = 5.13 Hz, H$^{6'}$); 7.27 (t, 1H, ^3J = 7.58 Hz, H^7); 7.15 (s, 1H, H$^{3'}$); 4.49 (q, 2H, ^3J = 7.09 Hz, -CH$_2$-CH$_3$), 1.45 (t, 3H, ^3J = 7.09 Hz, -CH$_2$-CH$_3$)

Keto form: 1-(9-ethyl-9*H*-carbazol-2-yl)-3-thieno[3,2-*b*]thiophen-2-ylpropane-1,3-dione. Chemical shifts of H^1, H^5, H^{3,4}, H$^{3'}$ cannot be distinguished from those of the enol form. δ = 8.24 (d, 1H, H^8); 7.78 (d, 1H, H$^{5'}$); 7.55 (d, 1H, H^{3,4}); 7.47 (d, 1H, H^6); 7.38 (d, 1H, H$^{6'}$); 7.24 (d, 1H, H^7); 4.76 (s, 2H, -CH$_2$-); 4.47 (q, 2H, -CH$_2$-CH$_3$), 1.42 (t, 3H, -CH$_2$-CH$_3$).

Preparation of sodium (1*Z*)-3-(9-ethyl-9*H*-carbazol-2-yl)-3-oxo-1-thieno[3,2-*b*]thiophen-2-yl-prop-1-en-1-olate (CTPD sodium salt). The deprotonated ligand was obtained as follows: 4 mg of the ligand were dissolved in ethanol (0.5 mL) in a 5 mL flask and 2 equivalents of sodium hydroxide were added (0.1 M in ethanol); the solution was stirred at rt for 1 h then the solvent was removed and the solid was dried under vacuum (0.3 mbar) for 2 h and then re-dissolved in the deuterated solvent (CD_3CN or THF-d_8).

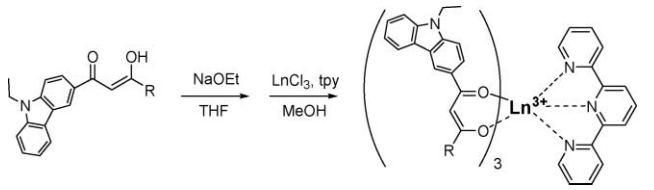
^{1}H-NMR (800 MHz in THF-d_8): δ = 8.78 (s, 1H, H^1); 8.17 (d, 1H, ^3J = 7.58 Hz, H^8); 8.14 (d, 1H, ^3J = 7.58 Hz, H^5); 7.87 (s, 1H, H^{enol}); 7.45 (d, 1H, ^3J = 7.33 Hz, H^{3,4}); 7.43 (d, 1H, ^3J = 5.13 Hz, H$^{5'}$); 7.38 (m, 2H, H^{3,4} and H^6); 7.23 (d, 1H, ^3J = 5.13 Hz, H$^{6'}$); 7.14 (t, 1H, ^3J = 7.33 Hz, H^7); 6.65 (s, 1H, H$^{3'}$); 4.40 (q, 2H, ^3J = 7.09 Hz, -CH$_2$-CH$_3$), 1.38 (t, 3H, ^3J = 7.09 Hz, -CH$_2$-CH$_3$)

Preparation of the CNPD ligand. 3-Acetyl-9-ethylcarbazole (1.50 g, 6.32 mmol) and methyl 2-naphthoate (1.40 g, 7.59 mmol) were dissolved in 50 mL anhydrous THF under a N_2 atmosphere. Sodium ethoxide (0.52 g, 7.59 mmol) was added. After stirring for 24 h at 60 °C, hydrochloric acid (1.0 N) was added to the solution. The crude mixture was extracted with CH_2Cl_2 and dried over anhydrous magnesium sulfate. The residue was purified by column chromatography (CH_2Cl_2) to give the final product as a yellowish solid. Yield: 81%; EI-MS calcd for $C_{27}H_{21}NO_2$ 391.16, Found [M$^+$] 391; Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found C, 82.76; H, 5.52; N, 3.52.

Enol form: (2*Z*)-1-(9-ethyl-9*H*-carbazol-2-yl)-3-hydroxy-3-naphthalen-2-yl-prop-2-en-1-one. δ = 9.01 (s, 1H, H^1); 8.72 (s, 1H, H^{enol}); 8.30 (dd, 1H, ^3J = 8.55 Hz, ^4J = 1.47 Hz, H$^{3',4'}$); 8.25 (d, 1H, ^3J = 7.58 Hz, H^8); 8.18 (dd, 1H, ^3J = 8.55 Hz, ^4J = 1.47 Hz, H$^{3',4'}$); 8.05 (d, 1H, ^3J = 7.83 Hz, H^{3,4}); 7.98 (d, 1H, ^3J = 8.55 Hz, H$^{8'}$); 7.94 (d, 1H, ^3J = 7.83 Hz, H^{3,4}); 7.62 (d, 1H, ^3J = 8.55 Hz, H$^{5'}$); 7.57 (m, 3H, H^5, H$^{6'}$ and H$^{7'}$); 7.49 (d, 1H, ^3J = 7.58 Hz, H^6); 7.43 (s, 1H, H$^{1'}$); 7.27 (d, 1H, ^3J = 7.58 Hz, H^7), 4.93 (s, 2H, -CH$_2$-, 0.02%),4.52 (q, 2H, ^3J = 7.34 Hz, -CH$_2$-CH$_3$), 1.44 (t, 3H, ^3J = 7.34 Hz, -CH$_2$-CH$_3$).

Preparation of sodium (2*Z*)-3-(9-ethyl-9*H*-carbazol-2-yl)-3-hydroxy-1-naphthalen-2-ylprop-2-en-1-olate (CNPD sodium salt). The product was synthesised with the same procedure as that reported for the CTPD sodium salt. δ = 8.82 (s, 1H, H^1); 8.52 (s, 1H, H^{enol}); 8.21 (d, 1H, ^3J = 8.56 Hz, H$^{8'}$); 8.17(d, 1H, ^3J = 8.32 Hz, H$^{3',4'}$); 8.12 (d, 1H, ^3J = 7.58 Hz, H^8); 7.88 (d, 1H, ^3J = 7.82 Hz, H^{3,4}); 7.79 (d, 1H, ^3J = 7.82 Hz, H^{3,4}); 7.77 (d, 1H, ^3J = 8.32 Hz, H$^{3',4'}$); 7.45 (d, 1H, ^3J = 7.33 Hz, H$^{5'}$); 7.38 (m, 4H, H^5, H^6, H$^{6'}$ and H$^{7'}$); 7.11 (t, 1H, ^3J = 7.58 Hz, H^7); 6.82 (s, 1H, H$^{1'}$); 4.39 (q, 2H, ^3J = 7.34 Hz, -CH$_2$-CH$_3$); 1.37 (t, 3H, ^3J = 7.34 Hz, -CH$_2$-CH$_3$).

Preparation of [Ln(diketonate)$_3$(tpy)][16]. General Procedure (see Scheme 2): a mixture of β-diketone (3.0 equiv.), and NaOEt (3.3 equiv.) was stirred in freshly distilled THF at room temperature overnight. After the completion of salt formation, the methanol solution of anhydrous $LnCl_3$ (1.0 equiv.) and terpyridine (1.1 equiv.) was added to the reaction solution, and then stirred for 2 days. The resulting solution was filtered and the solvents



Scheme 2 Synthesis of [Ln(diketonate)$_3$(tpy)] complexes (R = thieno[3,2-*b*]thiophene or naphthalene moiety).

were removed. The resultant solid was washed sequentially with methanol, diethyl ether and hexane, yielding a yellowish solid.

Preparation of [Er(CTPD)$_3$(tpy)]. A mixture of *β*-diketone (0.60 g, 1.49 mmol) and NaOEt (0.11 g, 1.64 mmol) was stirred overnight at rt in 50 mL distilled THF. After completion of the reaction, 10 mL of a methanolic solution of anhydrous $ErCl_3$ (136 mg, 0.50 mmol) and terpyridine (116 mg, 0.50 mmol) were added to the reaction solution, which was then stirred for 2 days. Yield 75%; Anal. calcd for $C_{84}H_{59}N_6O_6S_6Er$ and 1605.21: C, 62.74; H, 3.70; N, 5.23; S, 11.96; Er, 10.40, Found C, 60.80; H, 3.77; N, 4.99; S, 12.08; Er, 10.83.

[Er(CNPD)$_3$(tpy)] was prepared as **[Er(CTPD)$_3$(tpy)]**. Yield 69%; Anal. calcd for $C_{96}H_{71}N_6O_6Er$ and 1569.47: C, 73.35; H, 4.55; N, 5.35; Er, 10.64, Found C, 72.52; H, 4.37; N, 5.07; Er, 10.72.

Preparation of [Gd(CTPD)$_3$(tpy)]. A mixture of *β*-diketone (0.25 g, 0.62 mmol) and NaOEt (0.05 g, 0.75 mmol) in 50 mL distilled THF was stirred overnight at rt. After completion of the reaction, 10 mL methanolic solution of anhydrous $GdCl_3$ (54 mg, 0.21 mmol) and terpyridine (53 mg, 0.23 mmol) were added to the reaction solution, which was then stirred for 2 days. Yield 52%; Anal. calcd for $C_{84}H_{59}N_6O_6S_6Gd$ and 1597.21: C, 63.13; H, 3.72; N, 5.26; S, 12.04; Gd, 9.84, Found C, 62.65; H, 3.94; N, 4.98; S, 12.33; Gd, 10.02

[Gd(CNPD)$_3$(tpy)] was prepared as **[Gd(CTPD)$_3$(tpy)]**. Yield 60%; Anal. calcd for $C_{96}H_{71}N_6O_6Gd$ and 1561.47: C, 73.82; H, 4.58; N, 5.38; Gd, 10.07, Found C, 73.06; H, 4.65; N, 5.04; Gd, 10.18

Preparation of [Nd(CTPD)$_3$(tpy)]. A mixture of *β*-diketone (0.45 g, 1.12 mmol) and NaOEt (0.08 g, 1.23 mmol) was stirred in 70 mL distilled THF overnight at rt. After completion of the reaction, 10 mL methanolic solution of anhydrous $NdCl_3$ (93 mg, 0.37 mmol) and terpyridine (87 mg, 0.37 mmol) were added to the reaction solution, which was then stirred for 2 days. Yield 78%; Anal. calcd for $C_{84}H_{59}N_6O_6S_6Nd$ and 1581.19: C, 63.65; H, 3.75; N, 5.30; S, 12.14; Nd, 9.10, Found C, 62.86; H, 3.92; N, 5.44; S, 12.23; Nd, 8.97

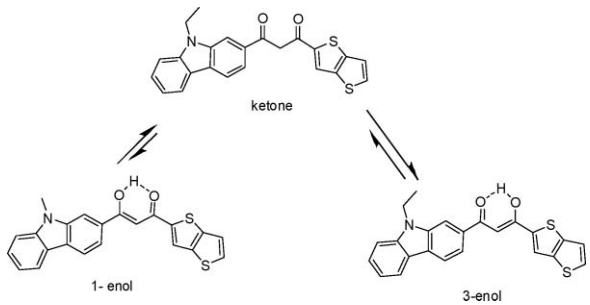
[Nd(CNPD)$_3$(tpy)] was prepared as **[Nd(CTPD)$_3$(tpy)]**. Yield 69%; Anal. calcd for $C_{96}H_{71}N_6O_6Nd$ and 1545.45: C, 74.44; H, 4.62; N, 5.43; Nd, 9.31, Found C, 74.17; H, 4.75; N, 5.49; Nd, 9.12.

Results and discussion

The two ligands, CTPD and CNPD were prepared in high yield from 3-acetyl-9-ethylcarbazole and the carboxylic acid derivative of the aromatic substituent. The corresponding one-pot synthesis is summarized in Scheme 1.

Structure and keto-enol ratio for CTPD and its deprotonated form, as determined by ^{1}NMR

β-Diketones exist as keto-enol tautomers.[10,11] Considerable attention has been focused on this equilibrium and it has been demonstrated that the ratio depends on the nature of the α-substituents, the polarity of the solvent, and the presence of acceptor or donor groups. In order to determine the structure of the CTPD and CNPD molecules, ^{1}H-NMR investigations have been conducted in different deuterated solvents for both the ligands and their deprotonated forms. Subsequently, the keto-enol ratios (see Scheme 3) have been estimated from the peak areas of the corresponding signals.



Scheme 3 Potential keto-enol structures for CTPD.

The NMR assignment of the molecular structures is based on 1D and 2D ^{1}H-NMR spectra recorded at 800 MHz. Each molecule exists in both its keto and enolic forms, the equilibrium being displaced in favour of one enol form in deuterated THF. The observed H^{enol} (-CH-) and H^{keto} (-CH_2-) peaks in CTPD appear as singlets at 8.30 ppm and 4.76 ppm (see Fig. 1). The chemical shifts observed for all protons are in agreement with the literature values.[17] Comparison of the integrated peak values of the CH_2 protons on the α-carbon points to the enolic form being the predominant molecular structure at room temperature. By integrating the area corresponding to both species the keto/enol ratio is found to be 5 : 95. The corresponding equilibrium constants in

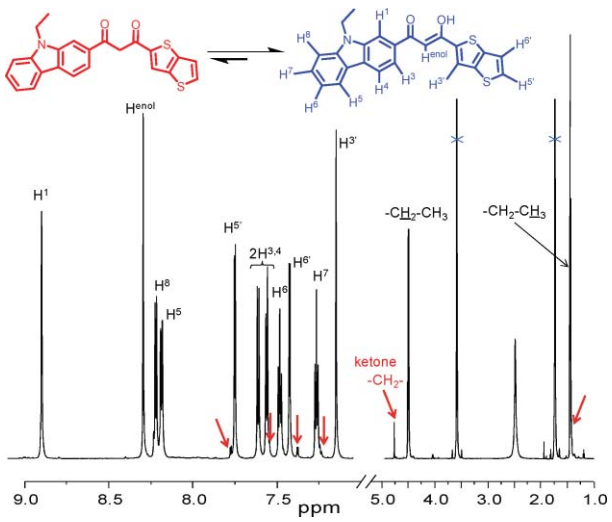


Fig. 1 ^{1}H-NMR spectrum CTPD ligand in THF-d_8. Resonances from the keto form are marked by red arrows.

deuterated THF-d_8 and CD_3CN were found to be 19.0 and 5.7 at rt, respectively.

As observed in the NMR spectrum, the most shielded aromatic protons in both keto and enol forms are those corresponding to the thieno[3,2-*b*]thiophen moiety ($H^{5'}$ and $H^{6'}$) which could indicate that the preferred enol form is (2*Z*)-**1**-(9-ethyl-9*H*-carbazol-2-yl)-**3**-hydroxy-3-thieno[3,2-*b*]thiophen-2-ylprop-2-en-1-one (1-enol) and not (2*Z*)-**3**-(9-ethyl-9*H*-carbazol-2-yl)-**3**-hydroxy-1-thieno[3,2-*b*]thiophen-2-ylprop-2-en-1-one (3-enol, see Scheme 3). When CTPD is dissolved in CD_3CN, the peaks are less resolved than in the previous case, but the keto form can still be clearly distinguished from the enol one and corresponds to *ca.* 15%.

If the ligand is totally deprotonated (by adding two equivalents of sodium hydroxide in ethanolic 0.1 M solution, stirring and evaporating the solvents), the observed form is the enol structure, whatever the solvent in which the experiment is conducted (THF-d_8 or CD_3CN), as shown in Fig. 2. All the protons are up-shielded compared to the spectrum of the protonated ligand. The most important chemical shift differences are observed for the enolate proton ($\Delta\delta = 0.43$ ppm) as could be expected, but the $H^{5'}$, $H^{6'}$ and $H^{3'}$ aromatic protons also display substantial shifts ($\Delta\delta =$ 0.50, 0.32 and 0.19 ppm, respectively, see Table 1). These protons belong to the thieno[3,2-*b*]thiophen moiety, which again indicates that the preferred enolate is in the C^3 and not the C^1 position.

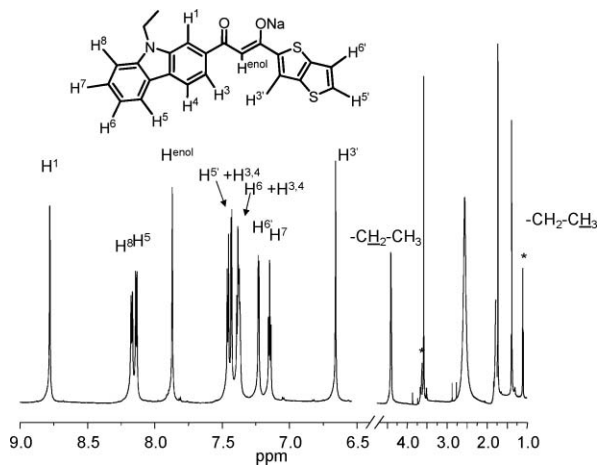


Fig. 2 ^{1}H-NMR spectrum of deprotonated CTPD in THF-d_8. * denote resonances from residual ethanol.

Structure and keto-enol ratio for CTPD and its deprotonated form, as determined by ^{1}NMR

The same experiments as for CNTP have been conducted with CNPD. The ligand is also essentially present under its enol form (1-(9-ethyl-9*H*-carbazol-2-yl)-3-(2-naphthalenyl)-1,3-propanedione (see Table 1 and Fig. 3). The keto form amounts to less than 2%, as calculated from the integrated intensity of the CH_2 singlet. The aromatic signals cannot be distinguished from those of the enol form. In deuterated acetonitrile, the CH_2 singlet is much more intense (5–10%), demonstrating that the equilibrium is slightly displaced in favour of the keto species in this solvent. This effect is smaller than the one observed for CTPD. After deprotonation of the ligand, the enol form is exclusively observed (see Fig. 4). Comparing the chemical shifts of the carbazolyl

Table 1 Chemical shift of the β-diketone ligands (HL) and their deprotonated forms (L^-) in THF-d_8

	CTPD			CNPD			δ_CTPD-δ_CNPD	
Proton	HL	L^-	$\Delta\delta$	HL	L^-	$\Delta\delta$	HL	L^-
H^1	8.90	8.78	0.12	9.01	8.82	0.19	–0.11	–0.04
$H^{3,4}$	7.61	7.45	0.16	8.05	7.88	0.17	–0.44	–0.43
$H^{3,4}$	7.56	7.38	0.18	7.94	7.79	0.15	–0.38	–0.41
H^5	8.18	8.14	0.04	7.57	7.38	0.19	0.61	0.76
H^6	7.49	7.38	0.11	7.49	7.38	0.11	0.00	0.00
H^7	7.27	7.14	0.13	7.27	7.11	0.16	0.00	0.03
H^8	8.22	8.17	0.05	8.25	7.58	0.67	–0.03	0.59
$H^{1'}$	/	/	/	7.43	6.82	0.61		
$H^{3'}$	7.15	6.65	0.50	8.3	8.32	–0.02		
$H^{4'}$	/	/	/	8.18	7.77	0.41		
$H^{5'}$	7.75	7.43	0.32	7.92	7.45	0.47		
$H^{6'}$	7.42	7.23	0.19	7.57	7.38	0.19		
$H^{7'}$	/	/	/	7.57	7.38	0.19		
$H^{8'}$	/	/	/	7.98	8.21	–0.23		
H^{enol}	8.30	7.87	0.43	8.72	8.52	0.2		
$-CH_2CH_3$	4.49	4.40	0.09	4.52	4.39	0.13		
$-CH_2CH_3$	1.45	1.38	0.07	1.44	1.37	0.07		

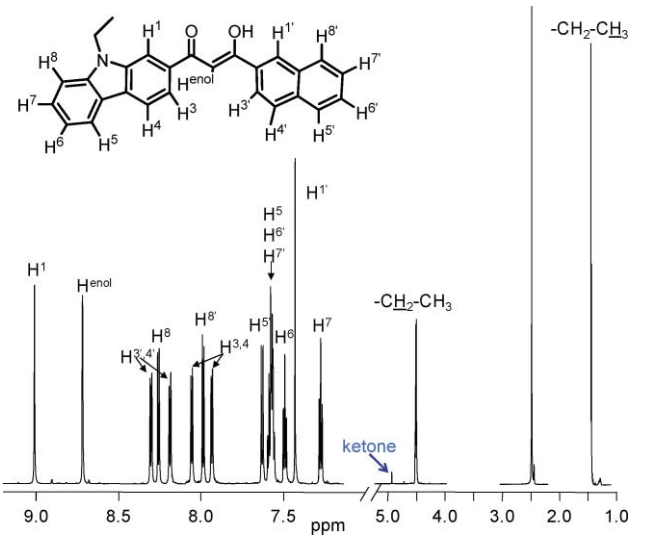


Fig. 3 ^{1}H-NMR spectrum of the CNPD ligand in THF-d_8. The signal from the keto form is indicated by an arrow. Large solvent resonances have been removed for clarity.

substituent in CTPD *vs.* CNPD shows that the H^3 and H^4 aromatic protons are down-shielded ($\Delta\delta = 0.4$ ppm) while H^5 is up-shielded ($\Delta\delta = 0.6$ ppm).

One the other hand, there is no influence on H^6 and H^7. A similar result is observed for H^8 when comparing the neutral ligand while a large effect occurs for the deprotonated form ($\Delta\delta = 0.6$ ppm). This is due to important electronic effects induced by the formation of the enolate. When comparing the protonated *vs.* deprotonated forms of CNPD, one sees that the carbazolyl aromatic protons are up-shielded by *ca.* 0.2 ppm, with the above-mentioned exception of H^8. On the other hand, the naphthalenyl moiety sustains much larger chemical shift displacements (Table 1), in particular for $H^{1'}$, $H^{4'}$, and $H^{5'}$. This indicates that the preferred enolate form is probably on C^3, thus inducing important electronic effects. The chemical behaviour of both ligands is then the same, the preferred enolate form being on the opposite side of the carbazolyl

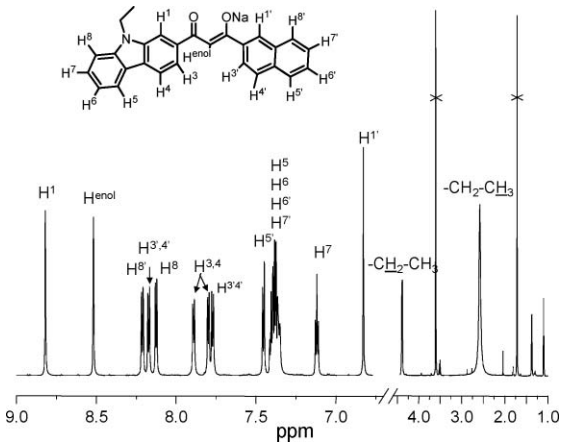


Fig. 4 ^{1}H-NMR spectrum of deprotonated CNPD in THF-d_8.

substituents. The keto-enol equilibria of push-pull chromophores are indeed affected by decreasing electron density at the α-position and substitution with bulky groups results in an increase of steric hindrance.[9,10] For these reasons the two β-diketones of this study appear mainly under the form of the *cis* enol tautomer, which is stabilized by conjugation and intramolecular hydrogen bonds.

Determination of the keto-enol ratios by HPLC

Complementary experiments have been conducted to check the keto-enol ratios of the neutral ligands. The latter were injected in water–acetonitrile solution and the gradient was adjusted to reach 100% MeCN in 100 min. In each case, two peaks appeared upon detection at 214 nm, the relative surface of them giving the keto-enol ratios. The results are in good agreement with those obtained previously by NMR spectroscopy (Table 2).

Photophysical properties of diketone ligands

Steady-state spectral properties. Absorption spectra of CTPD and CNPD in polar and non-polar solvents are shown in Fig. 5. CTPD and CNPD exhibit the absorption bands in the spectral ranges 250–350 nm and 350–450 nm. The former are attributable to the aromatic substituents, thieno[3,2-*b*]thiophene, naphthalene and carbazole groups.

The absorption bands around 350–450 nm are due to the conjugated β-diketone. The absorption maxima of CTPD and CNPD in polar solvent ($CHCl_3$, MeCN) are slightly red shifted compared to the absorption maximum in the non-polar solvent cyclohexane. As mentioned above, CTPD and CNPD exist in their keto and enol forms, the equilibria being displaced in favour of one enol form in polar THF-d_8 and CD_3CN. The conjugation length in the enol form is longer compared to the keto form. This

Table 2 Percentage of keto form present in CD_3CN and THF-d_8 for CTPD and CNPD as determined by NMR and HPLC

	NMR		HPLC (214 nm)
	THF-d_8	CD_3CN	MeCN
CTPD	5	15	12
Deprot. CTPD	0	0	/
CNPD	2	7	5
Deprot. CNPD	0	0	/

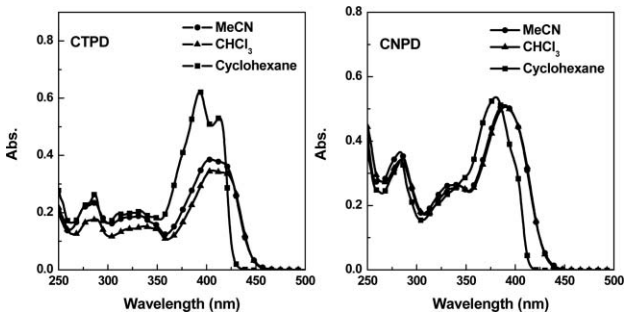


Fig. 5 UV-Vis absorption spectra of CTPD and CNPD in acetonitrile (MeCN), chloroform and cyclohexane.

indicates that CTPD and CNPD diketones are more conjugated in polar solvents. As a result, their absorption bands are red shifted in these solvents.

In contrast to weak solvent-dependence of the absorption spectra, the CTPD and CNPD ligands show remarkable solvatochromic emission behaviour as shown in Fig. 6. The fluorescence spectra of CTPD and CNPD in polar solvents display broad emission bands with large Stokes' shifts while those in non-polar cyclohexane exhibit a vibrational structure.[17] This may indicate that the nature of the excited electronic state in polar solvents is different. In addition, the phospholuminescence spectra of CTPD and CNPD in polar solvents are much alike, regardless of the excitation wavelength (Fig. S3, ESI†), indicating that the emissive states are similar.

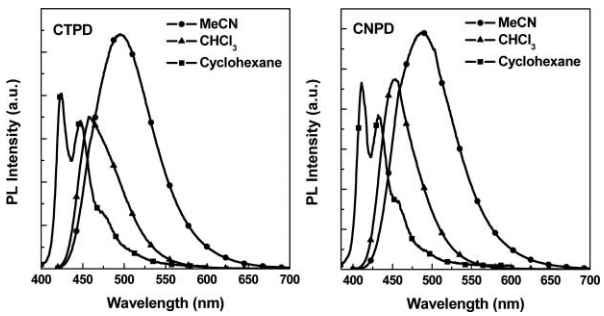


Fig. 6 Photoluminescence spectra of CTPD and CNPD.

The HOMO and LUMO orbitals of the two β-diketone derivatives have been calculated in order to evidence their electron donor–acceptor (push-pull) nature. Geometry optimization was carried out with the GAUSSIAN 03 W program, using the TD B3LYP method with a 6-31G(d) basis set.[18] The HOMO and LUMO orbitals are represented in Fig. 7. The characteristic feature of both HOMO orbitals is the π-density located on the carbazole moiety. Upon photoexcitation, one electron moves into the LUMO orbital, which results in the π-electronic density being transferred towards the fused thiophene and naphthalene moiety of CTPD and CNPD, respectively. Thus the theoretical modelling substantiates the fact that charge transfer does indeed take place between carbazole functioning as an electron donating group and the fused thiophene or naphthalene unit of the ligand enol forms acting as the accepting group. Intramolecular charge transfer processes usually generate large Stokes' shifts of the emission band in polar solvents.[12,19] This is in line with the structureless and red-shifted emission band detected in the absorption spectra in the

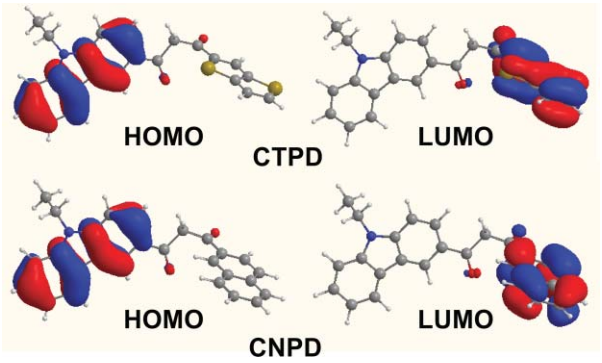


Fig. 7 HOMO and LUMO orbitals of β-diketone derivatives.

range 350–450 nm arising from the intra-ligand charge-transfer (ILCT) state.

Ligand-centred luminescence. In order to understand the excited state dynamics of CTPD and CNPD, we have measured the time-resolved fluorescence decays in various solvents upon excitation in the ILCT band around 390 nm. The fluorescence decay profiles were monitored at the emission maxima. The fluorescence decays of CTPD and CNPD in various solvents are mono-exponential and are depicted in Fig. S3–S5 (ESI†). The fluorescence lifetimes in cyclohexane are determined to be about 150 ps for both compounds. On the other hand, the fluorescence lifetime of CTPD and CNPD in a polar solvent such as MeCN increases 10-fold and reaches 1.5 ns, consistent with the fact that ILCT states of organic molecules generally exhibit a long decay time.[19] After deprotonation of the ligands, the observed lifetime is 1.78 ns for CTPD and 1.8 ns for CNPD in acetonitrile. As a conclusion, the structureless and red-shifted emission band in the fluorescence spectra of CTPD and CNPD in polar solvents as well as the increased excited state lifetimes ascertain the presence of ILCT states in these compounds.

The Gd(III) ion has no energy levels below 32 000 cm^{-1},[20] and the emission bands of CTPD are in the range 14300–25 000 cm^{-1}. Thus, Gd(III) cannot accept energy from the triplet or the singlet state of CTPD. In degassed MeCN, no significant phosphorescence is detected at room temperature for $[Gd(CTPD]_3(tpy)]$. However both a microcrystalline sample of this complex and the MeCN solution display a structured phosphorescence band at 77 K with a maximum at 520 nm (Fig. S6, ESI†). The luminescence decay of the solution is biexponential with corresponding lifetimes of 25.1 ± 0.3 ms (96%) and 1.88 ± 0.04 ms (4%). This may indicate a slight decomplexation in solution.

Metal-centred luminescence of $[Ln(CTPD)_3(tpy)]$ and $[Ln(CTPD)_3(tpy)]$ (Ln = Er, Nd). The NIR luminescence spectra of the Ln(III) complexes have been measured in acetonitrile. Upon excitation into the ILCT band of the ligands, the spectra of the Er(III) compounds display the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er(III) at 1530 nm.[21] The spectrum of $[Er(CTPD)_3(tpy)]$ is displayed in Fig. 8 as an example. Simultaneously, the emission intensity of the ligands is significantly diminished, compared to that of the corresponding free ligands. This may be ascribed to energy transfer from the ligands to the Er(III) ion. In Nd(III) complexes, weak and sharp Nd(III) emission bands in the NIR are assigned to the

Table 3 Lifetimes and quantum yields of the $[Ln(diket)_3(tpy)]$ complexes

sample	λ_{ex}/nm	λ_{an}/nm	T/K	τ_1/μs	Φ [%]
CTPD-Er	355	1530	295	1.44	0.008
CNPD-Er	355	1530	295	1.17	0.007
CTPD-Nd	355	1063	295	0.95	0.1
CNPD-Nd	355	1063	295	0.85	0.05

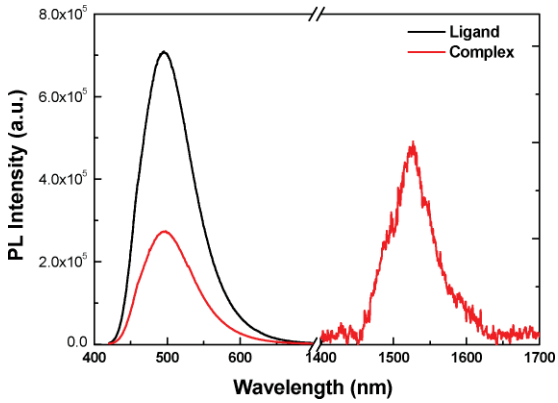


Fig. 8 NIR emission spectra of CTPD and $[Er(CTPD)_3(tpy)]$ 2.0×10^{-5} M in MeCN ($\lambda_{ex} = 410$ nm).

$^4F_{3/2} \rightarrow {}^4I_{9/2}$ (890 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1060 nm), and $^4F_{3/2} \rightarrow 4I_{13/2}$ (1340 nm) transitions, respectively (Fig. 9).[22] Upon laser excitation at 355 nm, time-resolved luminescence measurements showed that the lifetime of the Ln(III) excited states are in the range 1.17–1.44 μs for Er(III) complexes and 0.81–1.01 μs for Nd(III) complexes in aerated MeCN solution. The corresponding quantum yields were found to be 0.007–0.008% for the Er(III) complexes and 0.05–0.1% for the Nd(III) complexes (see Table 3).

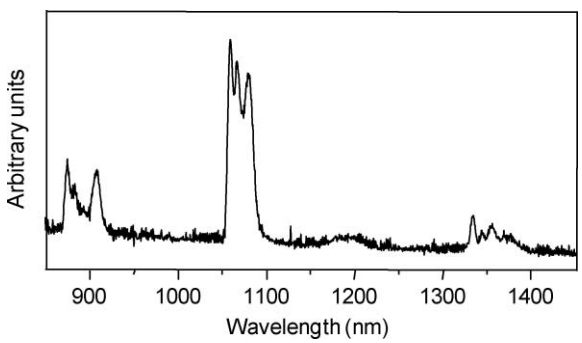


Fig. 9 Normalized NIR emission spectrum of a solid state sample of $[Nd(CTPD)_3]$ at 10 K ($\lambda_{ex} = 400$ nm).

Conclusions

The two new push-pull β-diketone chromophores fitted with charge-transport carbazole and aromatic moieties described in this study, CTPD and CNPD, essentially appear under the thermodynamically stable enol form in solution displaying extended resonance electronic structure: the *cis*-enol tautomer amounts to 95–98% of the speciation in THF at room temperature. These ligands possess an ILCT electronic state, the energy of which is sensitive to the polarity of the solvent and which allows convenient sensitization of the luminescence of NIR emitting ions such as

Nd(III) and Er(III) in the visible spectrum. Presently, the reported quantum yields for [Ln(diket)$_3$(tpy)] (Ln = Nd, Er; diket = CTPD, CNPD) remain modest in comparison with literature values[23] but modification of the ligand by removing the C–H vibration in the vicinity of the Ln(III) ion is feasible and should improve the photophysical properties of the tris complexes.

Acknowledgements

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