# Novel metal-template assembled highly-functionalized cyanoporphyrazine ytterbium and vanadium complexes for potential photonic and optoelectronic applications

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A novel facile synthetic route to the metal-template assembly of a tetrapyrrollic framework from tetracyanoethylene (TCNE) and tricyanovinylbenzene (TCNVB) structural units through reaction of TCNE and TCNVB with metal  $\pi$ -sandwich complexes has been developed. The reactions occur under extremely mild conditions, the porphyrazine macrocycles being assembled in high yield from TCNE and TCNVB building-blocks by VO<sup>2+</sup> or Yb<sup>3+</sup>-template synthesis. The redox behaviour of the novel complexes has been investigated. The vanadyl octacyanoporphyrazine complex was found to be a rare example of a highly-absorbing dye combining significant electron-acceptor properties with a band gap unusually narrow for an organic semiconductor (ca. 1.1 eV). The preparation is described of a novel highly emissive ytterbium complex with a proposed unusual structure obtained by reaction of TCNVB with bis(indenyl)ytterbium(II) in THF. The analytical, spectral and electrochemical investigations of the obtained ytterbium complex indicate it to be a binuclear adduct with Yb(TCNVB)<sub>3</sub> species in which a single doubly-reduced TCNVB molecule bridges two Yb3+ cations. The formation of a disordered polynuclear coordination polymer network including a macrocyclic structure and metal cations bridged through the nitrile nitrogen atoms is proposed. The complex is readily soluble and is compatible with a variety of polymeric matrices giving doped polymeric glasses and films which are highly luminescent in the biologically relevant optical window covering the visible and near-infrared (NIR) range (640–1000 nm). In addition, doped polymeric glasses and films highly emissive at the telecommunication wavelength (1540 nm), including a composition consisting of the novel ytterbium complex and an equimolar ratio of the novel ytterbium complex and a per se non-luminescent erbium chelate, have been obtained. The complex is found to be an extraordinarily strong sensitizer of NIR Er3+ emission.

# Introduction

Organic and organometallic semiconductors are very promising for a variety of photonic and optoelectronic applications.<sup>1,2</sup> They can show high absorption coefficients making them good chromophores for organic-based photovoltaic elements. On the other hand they can also possess intense luminescence over a wide range of wavelengths. The electronic band gap of organic semiconductors can be engineered by chemical design methods. Furthermore, organic semiconductors present advantages such as low-cost synthesis and easy manufacture of thin film devices by solution casting or printing technologies.

Recently, we reported a novel facile synthetic route for the metal template assembly of a tetrapyrrollic framework from TCNE structural units by the reaction of TCNE with  $\pi$ -sandwich metal complexes.3 This approach provided the first preparation of metalloporphyrazine dyes bearing eight peripheral strongly electron-withdrawing CN substituents (Fig. 1). Knowledge of the redox behaviour of these novel compounds should be of great interest from the aspects of both fundamental studies and practical applications. It motivated us to investigate the electrochemical properties of I and II and we report here the results of this study. Furthermore, we have applied this new synthetic method to other TCNE derivatives, and we also report here the preparation of two novel metal complexes designed from tricyanovinylbenzene (TCNVB) molecules as the structural units including an ytterbium tetracyanotetraphenylporphyrazine complex strongly luminescent over a wide range of wavelengths for which we propose an unusual binuclear structure IV.

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**Fig. 1** Structures of complexes prepared by reaction of  $V(C_6H_6)_2$  with TCNE (I) and with TCNVB (III) and by reaction of bis(indeny-l)ytterbium(II) with TCNE (II).

# Experimental

The starting material  $(C_9H_7)_2$ Yb $(THF)_2$  was synthesized by the method reported previously.<sup>4a</sup> V $(C_6H_6)_2$  was a commercial product (Cardinal Industries) additionally purified by sublimation. 2-(Phenyl)-1,1,2-tricyanoethylene (tricyanovinylbenzene, TCNVB), was synthesized according to the literature method<sup>4b</sup> and purified by sublimation. THF was distilled from sodium benzophenone ketyl; acetonitrile, benzene and toluene were distilled over P<sub>2</sub>O<sub>5</sub>. I·C<sub>6</sub>H<sub>6</sub>·3H<sub>2</sub>O and II·4CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>·3THF were synthesized according to previously published procedures.<sup>3</sup>

The UV/Vis spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer. Infrared spectra were taken on an FSM 1201 FT spectrophotometer by using Nujol mulls on NaCl plates or as KBr pellets. The steady-state fluorescence investigation was performed with a Perkin Elmer LS 55 luminescence spectrometer.

### Preparation of III · H<sub>2</sub>O

A solution of TCNVB (740 mg, 5.80 mmol) in THF (20 ml) was added to bis(benzene)vanadium(0) (154 mg, 1.45 mmol) under vacuum with stirring. The reaction mixture was kept for 2 h under vacuum and exposed to moist air for 5 h. The dark-green solution was separated, evaporated to dryness under vacuum, and the resulting residue was taken up in dry benzene. Careful removal of benzene under vacuum afforded **III** · **H**<sub>2</sub>**O** in 55% yield. IR (THF): 2200, 1619, 1596, 1562, 1260, 1158, 1098, 1036, 1014, 804, 757, 696. UV-vis (THF)  $\lambda_{max}$ , nm: 360, 645. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN, ppm)  $\delta$  7.1–7.7 (5H, m);  $\delta$  1.8–2.2 (2H (H<sub>2</sub>O), m). Elemental analysis found: C% 65.28, H% 2.98, N% 21.34, V% 6.70, calcd. for C<sub>44</sub>H<sub>22</sub>N<sub>12</sub>O<sub>2</sub>V: C% 65.92, H% 2.77, N% 20.97, V% 6.35. MALDI<sup>+</sup> *m*/*z*: 802 (M + H<sup>+</sup>), MALDI<sup>-</sup> *m*/*z*: 800 (M – H) where M = C<sub>44</sub>H<sub>22</sub>N<sub>12</sub>O<sub>2</sub>V.

### Preparation of IV · 8THF

A solution of TCNVB (442 mg, 2.5 mmol) in dry THF (10 ml) was added to bis(indenyl)ytterbium(II) ·2THF (270 mg, 0.5

mmol) in THF (2 ml). After 5 h the reaction mixture was extracted with dry THF affording a dark-blue solution which was separated and evaporated to dryness. The resulting residue was taken up in dry benzene. Careful removal of benzene under vacuum afforded **II** in 60% yield. IR (KBr): 2205, 2122, 1650, 1597, 1560, 1470, 1417, 1300, 1220, 1167, 1129, 1105, 1029, 765, 753, 743, 703, 682 cm<sup>-1</sup>. UV-vis (THF)  $\lambda_{max}$ , nm: 335, 400, 608, 1335. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN, ppm)  $\delta$  7.1–7.9 (5H, m);  $\delta$  1.81, 3.65–3.69 (8H (THF), m). Elemental analysis found: C% 60.38, H% 4.79, N% 13.45, Yb% 15.86 (EDAX), calcd. for C<sub>109</sub>H<sub>99</sub>N<sub>21</sub>O<sub>8</sub>Yb<sub>2</sub>: C% 60.13, H% 4.58, N% 13.51, Yb% 15.90.

### Preparation of doped polymer glasses

A solution of either **II** or a mixture of **II** with  $Er(Ac^FAc^F)_3$  in THF was added to a mixture of oligocarbonatedimethacrylate (M = 418.15) and 2,2-dimethoxy-phenylacetophenone as photoinitiator under intense stirring for 12 h in a vessel made of dark glass. After the formation of a transparent blue solution the THF was carefully removed under vacuum. The procedure of layer-by-layer UV polymerization was performed as described.<sup>4c</sup>

### Powder diffraction measurements

Data were collected in reflection mode on an R-Axis Rapid diffractometer using copper radiation, a graphite monochromator, and a 0.5 mm incident beam collimator.

### Time-resolved spectroscopy

For excitation of the investigated samples we used an Evolution-30 laser (Spectra Physics Lasers) delivering 100 ns pulses at 527 nm with a repetition rate of 1 kHz. The fluorescence spectra of the samples were measured by using a Princeton Instruments SpectraPro-2300 monochromator equipped with a Hamamatsu R4220 photomultiplier tube (PMT). The signal from the PMT was supplied by a Stanford Research SR830 lock-in amplifier. The time dependence of the fluorescence of the investigated samples was analyzed with an Agilent Technologies DSO6054A digital oscilloscope. PMT signals were acquired relative to sync pulses from the control unit of the laser. Excitation and fluorescence pulses were rejected and stored independently by using an appropriate colour optical filter set. The excitation pulse was deconvoluted from the fluorescence data to yield undisturbed decays which were fitted by an iterative least-squares procedure based on the conventional three-level model.

### **Electrochemical measurements**

Amperometric measurements were carried out by using a Voltalab PGZ100 potentiostat. A conventional three-electrode cell was used. The working electrode was an Au disk of diameter 0.5 mm inserted into a glass tube. The auxiliary electrode was a coiled Au wire. A classical calomel electrode saturated with KCl (SCE) was used as the reference, being connected to the cell through a separator assembly containing DMF and the supporting electrolyte tetrabutylammonium tetrafluoroborate. The electrolyte solution was purged with Ar gas for 30 min before each measurement to minimize oxygen concentrations. A blanket of Ar was maintained over the electrolyte solution during the

### Magnetic measurements

Magnetic measurements down to 2 K were carried out in a Quantum Design MPMS-XL-7T SQUID susceptometer. The magnetic investigations were performed on a polycrystalline sample. The molar susceptibility was corrected for the sample holder and for the diamagnetic contribution of all atoms by using Pascal's tables.<sup>44</sup>

### NIR luminescence registration

The luminescence spectra registration setup is shown in Fig. 2. A semiconductor laser 1 (ADL-66Z01HU, ARIMA



Fig. 2 The near-IR luminescence spectra registration setup.



Fig. 3 Cyclic voltammogram of complex I.

Optoelectronics; 20 mW) working in the cw mode at 660 nm was used as the pump source. The intensity-modulated pump radiation (516 Hz) was focussed through a hole in the ellipsoidal mirror 2 onto the sample 3. The sample emission was collected and focussed to the input split of the monochromator MDR-41 (LOMO) (4). In the wavelength range 800–1700 nm an InGaAsP p-i-n photodiode 5 was used as the receiver. The signal from the photoreceiver was recorded by the lock-in amplifier 6 and displayed with the computer 7.

### **Results and discussion**

The redox properties of complexes I-IV were investigated by cyclic voltammetry in DMF *vs.* SCE. The cyclic voltammograms (CV) for both complexes exhibit closed current–voltage loops showing that the electrogenerated intermediates are stable in the time-frame of the experiment. A typical CV for complex I is shown in Fig. 3.

The cyclic voltammetric behaviour of I shows that it is able to accept successively at least four electrons. A fairly well-defined reversible first reduction is observed at -0.08 V. This value of the formal first reversible reduction potential is unusually "positive" for a tetrapyrrollic macrocycle and its complexes. In particular, the vanadyl tetra-tert-butyl-porphyrazine metal complex has its first reduction potential 700 mV more negative than that for I.<sup>5</sup> Thus, the introduction of multiple strongly electron-withdrawing CN substituents into the porphyrazine peripheral framework has caused a remarkable increase in the electron-acceptor properties (Table 1). To the best of our knowledge the only previous example of a similar alteration in redox behaviour arising from the presence of peripheral substituents was that reported for Zn(II)and Ni(II) tetrakis(2,6-dichlorophenyl)-β-heptanitroporphyrines prepared by nitration of the corresponding tetrakis(2,6-dichlorophenyl)-porphyrines.<sup>6</sup> The first reduction step for I can be assigned, presumably, not to the macrocycle core but rather to the peripheral substituents since TCNE fragments framing the macrocycle, as has been noted,<sup>3</sup> partially retain the  $\pi$ -acceptor properties of free TCNE. The lowest unoccupied molecular orbital (LUMO) of I calculated from the linear relationship between the ionization and redox potentials of molecular organic semiconductors<sup>7a,b</sup> has an energy of 3.9 eV relative to free space.

In spite of its very high electron affinity, two irreversible oxidations at 0.71 and 0.94 V are also observed for **I**. The potentials given for these processes are the irreversible first and second anodic peaks in the CV trace. However, according to Forrest *et al.*,<sup>7a</sup> for materials exhibiting closed CV loops an irreversible peak potential can correspond to within 100 mV of the reversible oxidation potential. Thus, the energy *ca.* 5.0 eV

Table 1 Reduction and oxidation potentials vs. saturated calomel electrode (SCE) in DMF and molecular orbital energies of I, II, III and IV

Complex		Oxidation potentials/V	Molecular orbital energy/eV			
	Reduction potentials/V		НОМО	LUMO	Band gap	Q-band/nm
I	-0.08, -0.70, -1.28, -1.87	0.71, 0.94	-5.0	-3.9	1.1	678, 630
П	-0.39, -1.07, -1.26	1.19	-5.7	-3.6	2.1	672, 620 673, 610
IV	-1.21, -1.75	0.86, 1.41	-5.2	-2.2	3.0	582



Fig. 4 Absorption spectra of I (a), II (b) III (c) and IV (d) in THF.

estimated from the first oxidation potential (0.71 V) is also the energy of the highest occupied molecular orbital (HOMO) of I (Table 1). The energy difference between the HOMO and the LUMO, *ca.* 1.1 eV, is substantially lower than the energy of the long-wavelength  $\pi \rightarrow \pi^*$  transition (Q-band 1.83 eV) (Fig. 4a), so the oxidation is, presumably, metal-centred rather than occurring in the macrocycle. Interestingly, the value of the first oxidation potential of I is consistent with that for the vanadium (IV/V) redox couple (0.69 V *vs.* SCE) in vanadyl Schiff base complexes with electron-withdrawing NO<sub>2</sub> substituents (5-NO<sub>2</sub> Salen).<sup>8</sup>

The redox properties of complex II are very different from those of complex I exhibiting three reversible reductions and one irreversible oxidation (Table 1). The first reduction potential is substantially more negative for II (-0.39 V) than for I. This can be explained by the influence of the axial ligand, TCNE<sup>•-</sup>, which is able to donate to the porphyrazine  $\pi$ -orbital thus decreasing its electron affinity. The oxidation potential of II is also much higher than that for I since Yb<sup>III</sup>, unlike VO<sup>II</sup>, is inactive in the anodic processes so the oxidation of II, presumably, is macrocycle-centred. This is confirmed by the UV/visible spectrum of II. The energy difference between the first oxidation and reduction processes (2.1 eV) is comparable to the energy of the Q-band short wavelength shoulder energy (2.0 eV) (Fig. 4b).

Metal template assembly of the tetraphenyltetracyanoporphyrazine framework was achieved by using the same synthetic approach through reaction of TCNVB with bis(benzene)vanadium or bis(indenyl)ytterbium.

The reaction of the vanadium  $\pi$ -sandwich complex with TCNVB proceeds analogically to that with TCNE: a green solid soluble in THF and acetonitrile is formed in the presence of excess TCNVB after contact of the reaction mixture with air oxygen and moisture. Likewise, the compound has a typical

UV/visible absorption spectrum for porphyrazine metal complexes being very similar to the spectrum of I (Fig. 4c) and exhibiting Soret- and O bands with high molar absorbtivities at 358 nm (log  $\varepsilon = 4.6$ ) and 673 nm (log  $\varepsilon = 4.3$ ), respectively. A shoulder to lower wavelength at ca. 610 nm can be attributed to a vibronic overtone according to Gouterman's four orbital model. The IR spectrum of the complex exhibits pyrrole vibration bands ( $v_{C=N}$  1654 cm<sup>-1</sup>, 1619 cm<sup>-1</sup>,  $v_{C=C}$  1597 cm<sup>-1</sup>, 1561 cm<sup>-1</sup>), the typical skeletal stretching of the porphyrazine macrocycle at 1490 cm<sup>-1</sup> and also  $v_{VO}$  at 980 cm<sup>-1</sup>. In the C $\equiv$ N stretch region only a single band at 2204 cm<sup>-1</sup> is observed. This band differs from  $\nu_{C\equiv N}$  in free TCNVB (2233 cm  $^{-1})$  and so can be assigned to the CN groups belonging to the TCNB fragments at the periphery of the macrocycle analogically to that in the vanadyl octacyanoporphrazine complex (Table 2).<sup>3</sup> Elemental analysis of the purified product gives the empirical formula  $III \cdot H_2O$  in excellent agreement with the mass-spectrometry results. The MALDI<sup>-</sup> and MALDI<sup>+</sup> spectra displayed isotopic clusters at m/z = 800 and m/z = 802, respectively, corresponding to the ions  $[M - H]^-$  and  $[M + H]^+$ , where  $M = III \cdot H_2O$ .

The substitution of four cyano groups by phenyls causes a strong decrease in the complex electron affinity (Table 1). Furthermore, like **II** but unlike **I**, the first oxidation of complex **III** may be assumed to be a macrocycle-centred process since its band gap (2 eV) is rather close to the Q-band energy of **III** (610 nm).

It should be noted that, in principle, four possible isomers of **III** with a different distribution of CN and Ph groups at the macrocycle periphery can be formed. For the sake of clarity only isomer **III** with alternating peripheral Ph and CN groups is presented in Fig. 1.

The analogous reaction of TCNVB with the ytterbium  $\pi$ -sandwich complex (bis(indenyl)ytterbium (II)) proceeds very smoothly under vacuum with the formation of a dye-like darkblue product (IV) readily soluble in THF and acetonitrile. In contrast to III which is rather unstable in the air rapidly changing colour from green to brown in solution, the Yb-containing product is very stable not only in the solid state but also in solution. The IR spectrum of the ytterbium complex shows porphyrazine macrocycle skeletal (ca. 1470 cm<sup>-1</sup>) and pyrrole ring stretching vibration bands ( $v_{C=N}$  1650 cm<sup>-1</sup>,  $v_{C=C}$  1597, 1560 cm<sup>-1</sup>). In the C $\equiv$ N stretch region a band at 2205 cm<sup>-1</sup> which can be assigned to the CN groups belonging to the TCNVB fragments at the periphery of the macrocycle is additionally observed as is also the case for I-III. The UV/visible electronic absorption spectrum (Fig. 4d) is also rather typical for porphyrazine metal complexes, particularly for those containing extra ligands in the axial position of the macrocycle, exhibiting absorption bands at 582 nm (Q-band) and 324 nm (Soret band). Furthermore, the spectrum shows an additional electronic transition in the visible region at 393 nm. Lower intensity absorptions

**Table 2** Summary of  $v_{C \equiv N}$  data for I–IV, TCNE, TCNVB and their radical-anions

Compound	I	П	III	IV	TCNE <sup>10</sup>	TCNVB	TCNE radical-anion <sup>10</sup>	TCNVB radical-anion
$v_{C\equiv N} (cm^{-1})$	2215 (s)	2210 (s) 2144 (m,br)	2204 (s)	2204 (s,br) 2122 (s,br)	2262 (s) 2228 (m) 2214 (w)	2234 (s)	2183 (m) 2144 (m)	2195 (m) 2185 (sh) 2122 (s)

of porphyrazine metal complexes in the optical window between the Q and Soret bands are usually assigned to charge-transfer (CT) transitions,  $Yb \rightarrow$  macrocycle and/or axial ligands.<sup>9</sup>

The presence of a reduced form of TCNVB as an axial ligand is consistent with the IR spectrum of the purified ytterbium complex showing additional  $C \equiv N$  stretch bands at 2122 cm<sup>-1</sup>. We observed the same frequency for the  $C \equiv N$  stretch bands for the product of TCNVB reduction on a potassium mirror in THF (Table 2). It should be noted, however, that the  $v_{C=N}$  band in the ytterbium complex is greatly broadened (half-width at halfheight *ca*. 60 cm<sup>-1</sup> *cf. ca*. 15 cm<sup>-1</sup> for free TCNVB<sup>•-</sup>) consistent with the TCNVB reduced forms being bound to ytterbium in the axial position. Interestingly, we did not observe any TCNVB<sup>•-</sup> ESR signal for IV: this may be explained by presence of electron delocalization within the complex.

Electrochemical investigations of IV revealed an appropriate decrease in reduction potential as a result of the replacement of four peripheral cyano groups by four phenyl groups (Table 1). The first reduction potential of IV (-1.21 V) is consistent with the second reduction potential for free TCNVB confirming the presence of TCNVB<sup>•-</sup> which can undergo reduction in the complex.<sup>11</sup> Thus, a structure analogous to II might be expected for the TCNVB based ytterbium complex. However, such a structure was not confirmed by the elemental analysis data. Substantial differences between the two complexes can also be deduced from a comparison of their redox properties (Table 1).

We observed for the TCNVB-based Yb complex two irreversible oxidation potentials at 0.86 and 1.41 V. Neither oxidation can be assigned to the metal since Yb<sup>3+</sup> is inactive in the anodic processes nor can they be assigned to the macrocycle since the energy of the Q band (2.13 eV) is much lower than the energy difference between the HOMO and LUMO (3.0 eV). The latter band-gap is very close to 393 nm which is consistent with the absorption band we observed in the optical window between the Q and Soret bands, i.e. for charge-transfer between the transition metal and the axial ligand. Thus, it is reasonable to assume that the first and second oxidation potentials correspond to oxidation of doubly and singly reduced TCNVB species, respectively. This is not inconsistent with the IR data showing two  $v_{C=N}$  bands for IV attributed to the macrocycle and CN radical-anion groups: both bands are very broad and may obscure the bands corresponding to the dianion CN.

In turn, the presence of doubly reduced TCNVB allows one to postulate the formation of binuclear species formed by its bridging at least two Yb atoms. Such an assumption is consistent with the presence of the strong broad absorption band in the near IR region with a maximum at 1335 nm (Fig. 5) very typical for binuclear structures. It is known that bi- and polynuclear complexes containing bridging TCNE ligands have intense absorption bands in the NIR region (800–1500 nm) corresponding, for example, to  $\pi \rightarrow \pi^*$  transitions of polymetal-containing systems in a delocalized description.<sup>12</sup>

Indeed, assumption of the formula  $[Ybpz(Ph)_4(CN)_4] \cdot \mu$ -[Ph(CN)C=C(CN)\_2] · Yb[Ph(CN)C=C(CN)\_2]\_2 (IV) for the binuclear adduct formed in the system bis(indenyl)ytterbium(II)– TCNVB gives excellent agreement with the elemental analysis results. It should be noted that chemical and NMR analysis also showed the presence of 6–8 molecules of THF in adduct IV.



Fig. 5 Near IR absorption of thin film of complex IV.

Adduct IV can be described as the final product of two processes resulting from oxidation of the bis(indenyl)ytterbium(II) sandwich  $\pi$ -complex with TCNVB: the metal template assembly of the porphyrazine macrocycle and the formation of Yb(TCNVB)<sub>3</sub>. It should be noted that a species similar to the latter,  $Ln(TCNE)_3$ , (Ln = Gd, Dy), has been observed previously by Raebiger and Miller.13 However, in spite of numerous attempts, we have been unable to obtain crystals of IV presumably because of its polymeric nature. In addition, a mixture of at least 4 isomers resulting from the distribution of phenyl and cyanide substituents should be formed. Powder diffraction measurements showed complex IV to be amorphous and in the absence of X-ray structural data the binuclear bridging structure can only be tentative (Fig. 6). The fragment of Ln(TCNVB)<sub>3</sub> is assumed to form a disordered polynuclear coordination polymer network with metal cations bridged through the nitrile nitrogen atoms.

The MALDI spectrum of IV shows a large number of peaks corresponding to ionic species containing more than one ytterbium atom including the ionic cluster with a maximum at m/z



Fig. 6 Proposed structure for complex IV (single isomer shown for clarity).



**Fig.** 7 Results of magnetic studies on **IV**:  $\chi^{-1}$  vs. *T* and  $\chi T$  vs. *T* plots (see text).

1636 for the  $[M - {Ph(CN)C=C(CN)_2} - H]^+$  ion where  $M = IV \cdot 3THF$ .

Magnetic measurements have been made on IV from 2 to 300K under a magnetic field of 5000 Oe. As expected from the proposed structure (Fig. 6), this compound displays paramagnetic behaviour indicating that the ytterbium atoms are present as Yb(III) ions in the complex. The  $\chi T$  value recorded at 300 K was 4.71 cm<sup>3</sup> K mol<sup>-1</sup> being somewhat smaller than the expected value for two isolated Yb(III) centres (5.12 cm<sup>3</sup> K mol<sup>-1</sup>).<sup>14a</sup> This may be explained by the antiferromagnetic interactions between the TCNVB radical anions and the Yb(III) centre. The  $\chi^{-1}$  vs. T curve (Fig. 7) follows rather well the expected shape for two weakly interacting Yb(III) centres with the observation of two linear regions (2-40 K and 65-300 K) with different slopes.14a Weak antiferromagnetic interactions are seen in the low temperature region, all the paramagnetic centres (Yb(III) and radical-anions) appearing to be weakly antiferromagnetically coupled. However, a comparison of the magnetic behaviour of IV with that of previously reported<sup>14b,c</sup> 2:1 metal-toligand neutral adducts  $(Cp*_2Yb)_2(\mu-L)$ , where L are dianionic/ diamagnetic bridging ligands, indicates that IV may be composed of binuclear adducts in which the bridging ligand does not facilitate significant magnetic exchange between the two Yb(III) centres at low temperatures. Indeed, such behaviour is rather typical for binuclear adducts where L has a free ligand second reduction potential which is less negative than ca. -2.0 V vs. SCE (cf. ca. -1.2 V for TCNVB<sup>11</sup>) when the energy of the ligand LUMO is not properly poised to facilitate metal-metal electronic interaction.14d

Similarly to the other cyanoporphyrazine complexes reported previously,<sup>3</sup> adduct IV readily forms optically-transparent solid solutions and films with various polymers such as polyethylcyanoacrylate, polyacrylonitrile, conjugated polycarbosilanes and others. But the most interesting feature of IV is the extraordinary light-emitting properties of this compound incorporated into solid polymer matrices. For example, high optical quality luminescent polymer films and glasses ( $100 \times 50$  $\times$  2.3 mm) have been prepared from UV-polymerized oligocarbonatedimethacrylate (PCMA) doped with 10<sup>-5</sup> and 10<sup>-4</sup> mol  $1^{-1}$  of IV (Samples 1 and 2, respectively). They reveal an intense visible and NIR photoluminescence dependent on the dopant concentration and the excitation wavelength.



Excitation with light in the wavelength range 530–600 nm gives intense visible luminescence at 650 nm. This emission can be readily observed under visible light for the doped glasses (Fig. 8; see Table of Contents for colour version).

The emission and excitation spectra of Sample 1 (Fig. 9) show a small Stokes shift that is very typical for dye fluorescence. Time-resolved spectroscopy was used for the luminescence life time measurements. For excitation we used an Evolution-30 laser (Spectra Physics Lasers) delivering 100 ns pulses at 527 nm with a repetition rate of 1 kHz. The short luminescence life-time (6.6 ns for Sample 1 and 5.1 ns for Sample 2) defined from the emission pulse delay with respect to the excitation pulse also



**Fig. 8** PCMA luminescent glass doped with  $10^{-4}$  mol  $1^{-1}$  of **IV** (Sample 2) (a) in transmitted light; (b) in reflected light (see Table of Contents for colour version).



**Fig. 9** Excitation ((a),  $\lambda_{\text{reg}} = 650 \text{ nm}$ ) and emission ((b),  $\lambda_{\text{excit}} = 590 \text{ nm}$ ) spectra of Sample 1 (10<sup>-5</sup> mol l<sup>-1</sup> IV).



**Fig. 10** Time dependence of the excitation (solid line) and fluorescence (dot/dash lines) pulses (arbitrary units).

confirmed that the luminescence at 630–650 nm originates in the porphyrazine framework arising from the  $\pi \rightarrow \pi^*$  electron transition in the porphyrazine ligand with the first singlet macrocycle excited state (S<sub>1</sub>) decaying back to the ground singlet state (S<sub>0</sub>) (Fig. 10). The quantum yield of the fluorescence peak with a maximum at 650 nm measured relative to Rhodamine 6G ethanol solution (0.95)<sup>15</sup> is about 0.13.

A substantial dependence of emission on the dopant concentration was found for the PCMA doped glasses. In the timeresolved emission spectrum we observe the fluorescence maximum occurring at a longer wavelength region for Sample 2 which is one order of magnitude more concentrated than Sample 1 (Fig. 11). In turn, the investigation by steady-state luminescence of Sample 2 (Fig. 12a) showed the appearance of an additional emission band strongly shifted to the NIR region (710 nm). Furthermore, the appearance of an anti-Stokes luminescence band at about 450 nm in this spectrum is of particular interest suggesting an increase in photon-phonon energy transfer in the system that can be indirect evidence for the presence of a disordered coordination polymer network formed by Yb[Ph(CN)C=C(CN)<sub>2</sub>]<sub>3</sub> fragments. The contribution of the supramolecular interactions in such a network into energy transfer processes should obviously increase with the complex concentration.



Fig. 12 The steady-state emission spectra of Sample 2, (a)  $\lambda_{\text{excit}} = 590$  nm; (b)  $\lambda_{\text{excit}} = 660$  nm.

The change of excitation wavelength to 660 nm resulted in luminescence only in the NIR (Fig. 12(b)). In addition to emission at 700 nm, intense NIR luminescence at 977 nm appears in Sample 2 (Fig. 13). This emission is attributed to narrow-bandwidth emission derived from the Yb  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition. It is a typical example of "antenna"-type excitation, where energy is transferred from the excited state of the ligand moiety to the emissive f-excited state of the lanthanide.

Furthermore, additional doping of the composite containing  $10^{-4}$  mol l<sup>-1</sup> of complex **IV** with an erbium chelate (erbium trishexafluoroacetylacetonate,  $Er(Ac^FAc^F)_3$ ), Yb:Er molar ratio = 1:1 (Sample 3), results in the appearance of an additional significant emission in the NIR region at 1540 nm (minimum-loss transmission window of silica fibre in optical telecommunication networks) and can be attributed to the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition of  $Er^{3+}$  (Fig. 14).

This phenomenon is not surprising since  $Yb^{3+}$  is a well-known  $Er^{3+}$  emission sensitizer with a relatively strong absorption at *ca.* 975 nm, the  ${}^{2}F_{5/2}$  level of  $Yb^{3+}$  and the  ${}^{4}I_{11/2}$  level of  $Er^{3+}$  being nearly resonant in energy.<sup>16</sup> On the other hand it is known that in the sensitization process of  $Er^{3+}$  luminescence by  $Yb^{3+}$ , the  $Er^{3+}\cdots$   $Yb^{3+}$  distance plays a significant rôle: the shorter the  $Er^{3+}\cdots Yb^{3+}$  distance the more effective the sensitization.<sup>13</sup> Thus, it is reasonable to assume that as a result of ligand exchange



Fig. 11 Time-resolved fluorescence spectra of Samples 1, 2 and 3 in arbitrary units ( $\lambda_{\text{excit}} = 527 \text{ nm}$ ).



Fig. 13 NIR photoluminescence spectrum of Sample 2 ( $\lambda_{\text{excit}} = 660 \text{ nm}$ ).



Fig. 14 NIR photoluminescence spectrum of Sample 3 doped with  $Er(Ac^{F}Ac^{F})_{3}$ , (Yb and Er complex molar ratio 1:1),  $\lambda_{excit} = 660$  nm.

Er(Ac<sup>F</sup>Ac<sup>F</sup>)<sub>3</sub> can be incorporated into the coordination polymer network formed by the Yb(TCNVB)<sub>3</sub> fragment of IV. This causes the short distance between the Yb and Er cations and facilitates intramolecular Yb-Er energy-transfer. It should be noted that no luminescence whatsoever of Er(AcFAcF)<sub>3</sub> in a PCMA matrix is observed in the absence of IV. Thus, it may be expected that "antenna"-type excitation applied to IV is more efficient for energy transfer to Er<sup>3+</sup> than is the direct excitation of Yb<sup>3+</sup> applied in the recently reported erbium vtterbium co-crystalline complexes exhibiting an increase of as much as ca. 30% in Er<sup>3+</sup> emission in comparison with the neat erbium complex.<sup>17</sup> We report here the first example, to our knowledge, of a lanthanide porphyrazine complex exhibiting NIR emission of Yb<sup>3+</sup> and efficiently sensitizing the emission of Er<sup>3+</sup>. Only one other example of NIR emissive ytterbium and erbium complexes (with an Yb<sup>3+</sup> and Er<sup>3+</sup> emission quantum yield ratio of *ca.* 30:1) based on a tetrapyrrole macrocycle (tetraphenylporphyrine) has been reported previously.18

# Conclusions

The series of new vanadyl and ytterbium(III) cyano-substituted porphyrazine complexes designed from TCNE and TCNVB structural units through reaction of TCNE and TCNVB with metal  $\pi$ -sandwich complexes has been developed. The influence of the nature of the central metal cation and the macrocycle peripheral framework on the redox behaviour and structure of the complex have been demonstrated. The vanadyl octacyanoporphyrazine complex was found to be a rare example of a highly-absorbing dye combining significant electron-acceptor properties with a band gap unusually narrow for an organic semiconductor (ca. 1.1 eV). The preparation is described of a novel highly emissive ytterbium complex, for which an unusual structure is proposed, obtained by reaction of TCNVB with bis(indenyl)ytterbium(II) in THF. The analytical, spectral and electrochemical investigations of the ytterbium complex thus obtained indicate that it exists in the form of a binuclear adduct consisting of an Yb(TCNVB)<sub>3</sub> species in which a single doublyreduced TCNVB molecule bridges two Yb3+ cations. The formation of a disordered polynuclear coordination polymeric

network with a macrocyclic structure and metal cations bridged through the nitrile nitrogen atoms is proposed. The complex is readily soluble and is compatible with a variety of polymeric matrices giving doped polymeric glasses and films which are highly luminescent in the biologically relevant optical window covering the visible and NIR range (640-1000 nm). In addition, doped polymeric glasses and films highly emissive at the telecommunication wavelength (1540 nm), including a composition consisting of the novel ytterbium complex and an equimolar ratio of the novel ytterbium complex and a per se non-luminescent erbium chelate, have been obtained. The complex is found to be an extraordinarily strong sensitizer of NIR Er<sup>3+</sup> emission. The materials developed based on novel porphyrazine vanadyl and ytterbium complexes formed in high yield by metal-template assembly from TCNE and TCNVB building-blocks have promising potential in modern photonic and optoelectronic devices such as photovoltaic cells, IR amplifiers in photonic integrated circuits, NIR emission sources in telecommunication defence applications and bio-imaging.

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### References

- 1 S. R. Forrest, Organic Electronics, 2003, 4, 45-48.
- 2 S. Gunes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, 107, 1324–1338.
- 3 L. G. Klapshina, I. S. Grigoryev, W. E. Douglas, A. A. Trifonov, I. D. Gudilenkov, V. V. Semenov, B. A. Bushuk and S. B. Bushuk, *Chem. Commun.*, 2007, 1942–1944.
- 4 (a) A. A. Trifonov, E. A. Fedorova, V. N. Ikorskii, S. Dechert, H. Schumann and M. N. Bochkarev, *Eur. J. Inorg. Chem.*, 2005, 2812–2818; (b) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Am. Chem. Soc.*, 1958, **80**, 2815–2822; (c) V. M. Treushnikov, *J. Photochem. Photobiol. A: Chemistry*, 2008, **196**, 201–209; (d) O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
- 5 N. Kobayashi, S. Nakajima and T. Osa, Chem. Lett., 1992, 2415-2418.
- 6 K. Ozette, P. Leduc, M. Palacio, J.-F. Bartoli, K. M. Barkigia, J. Fager, P. Battioni and D. Mansuy, J. Am. Chem. Soc., 1997, 119, 6442–6443.
- 7 (a) B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov and M. E. Thompson, *Organic Electronics*, 2005, 6, 11–20; (b) C. Borek, K. P. Hanson, I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski and J. Brown, *Angew. Chem. Int. Ed.*, 2007, 46, 1109–1112.
- 8 A. H. Kianfar and S. Mohebbi, J. Iran. Chem. Soc., 2007, 46, 1109–1110.
- 9 P. A. Stuzhin, S. I. Vagin and M. Hanack, *Inorg. Chem.*, 1998, 37, 2655–2662.
- 10 J. S. Miller, Angew. Chem. Int. Ed., 2006, 45, 2508-2525.
- 11 H. Bock, W. Seitz, N. Nagel, R. Baur, J. W. Bats, Z. Havlas and R. F. C. Claridge, *Zeit. fur Naturforsch.*, B: Chem. Sci., 1997, 52, 1125–11383.
- 12 (a) R. Gross-Lannert, W. Kaim and B. Olbrich-Deussner, *Inorg. Chem.*, 1990, **29**, 5046–5053; (b) W. Kaim and M. Moscherosch, *Coord. Chem. Rev.*, 1994, **129**, 157–193; (c) C. Diaz and A. Arancibia, *Polyhedron*, 2000, **19**, 137–145.

- 13 J. W. Raebiger and J. S. Miller, *Inorg. Chem.*, 2002, **41**, 3308-3312.
- (a) M. Schultz, J. M. Boncella, D. J. Berg, T. D. Tilley and R. A. Andersen, Organometallics, 2002, 21, 460; (b) C. N. Carlson, C. J. Kuehl, R. E. da Re, J. M. Veauthier, E. J. Schelter, A. E. Milligan, B. L. Scott, E. D. Bauer, J. D. Thompson, D. E. Morris and K. D. John, J. Am. Chem. Soc., 2006, 128, 7230– 7241; (c) D. J. Berg, J. M. Boncella and R. A. Andersen, Organometellics, 2002, 21, 4622–4631.
- 15 R. F. Kubin and A. N. Fletcher, J. Luminesc., 1982, 27, 455-462.
- 16 M. P. Hehlen, N. J. Cockroft, T. R. Gosnell and A. J. Bruce, *Phys. Rev. B*, 1997, 56, 9302.
- 17 L. Song, X. Liu, Z. Zhen, C. Chen and D. Zhang, J. Mater. Chem., 2007, 17, 4586–4590.
- 18 (a) B. S. Harrison, T. J. Foley, A. S. Knefely, J. K. Mwaura, G. B. Cunningham, T.-S. Kang, M. Bouguettaya, J. M. Boncella, J. R. Reynolds and K. S. Schanze, *Chem. Mater.*, 2004, 16, 2938– 2947; (b) T. J. Foley, B. S. Harrison, A. S. Knefely, K. A. Abboud, J. R. Reynolds, K. S. Schanze and J. M. Boncella, *Inorg. Chem.*, 2003, 42, 5023–5032.