Metal template assembly of highly functionalized octacyanoporphyrazine framework from TCNE structural units†

Larisa G. Klapshina,*[a] Ilya S. Grigoryev,[a] William E. Douglas,[b] Alexander A. Trifonov,[a] Ivan D. Gudilenkov,[a] Vladimir V. Semenov,[a] Boris A. Bushuk[c] and Sergey B. Bushuk[c]

Received (in Cambridge, UK) 8th February 2007, Accepted 15th March 2007
First published as an Advance Article on the web 3rd April 2007
DOI: 10.1039/b701994g

A new route to the octacyanoporphyrazine framework based on the interaction of metal sandwich π-complexes with TCNE has been developed.

Tetracyanoethylene (TCNE) is a very important starting compound in modern synthetic and materials chemistry. The great variety of its numerous reaction modes and chemical versatility have been surveyed in a very recent fundamental review by Miller.[1a] It was particularly emphasized that a wide array of products based on TCNE is available and that the understanding of their structures and properties is very challenging. Here, we report a new macrocyclic structure designed from TCNE molecules as the structural unit by a template synthesis involving vanadyl or Yb^{3+} ions.

We have found that the interaction of TCNE with bis(arene)-vanadium in acetonitrile, extensively described previously,[1a,b,c] can have an unexpected sequel when the reaction mixture is allowed to contact air and moisture. Within an hour the black suspension formed under vacuum by interaction of bis(benzene)vanadium and TCNE in acetonitrile at room temperature is converted to a deep green solution. The product of the reaction was purified from excess TCNE and arene ligand by washing with benzene which binds free TCNE by formation of a charge transfer complex. The purification was presumed to be complete when the aromatic hydrocarbon extracts were colourless and the very strong IR band of free TCNE ($\nu_{C\equiv N}$ 2260 nm) was absent. After careful removal of benzene by heating the product under vacuum a dark green solid soluble in THF, acetonitrile, DMF and DMSO was obtained in 50–60% yield (ESI). The ESR spectrum of an acetonitrile solution showed an anisotropic signal with $g_{\parallel} = 1.960$, $a_{\parallel} = 175$ and $g_{\perp} = 1.978$, $a_{\perp} = 56$ characteristic of vanadyl porphyrazine complexes.[2] The presence of the porphyrazine macrocycle is also confirmed by the typical electronic absorption spectrum (Fig. 1a(A)) showing intense Soret and Q bands, assigned as $\pi \rightarrow \pi^*$ transitions, at 395 nm and 680 nm, respectively (with a shoulder to lower wavelength at *ca.* 620 nm which can be attributed to a vibronic overtone according to Gouterman's four orbital model[3]). All the bands exhibit very high molar absorptivities (log $\varepsilon = 4.3$) typical of all porphyrazine dyes.

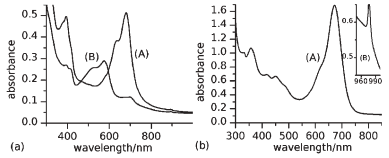
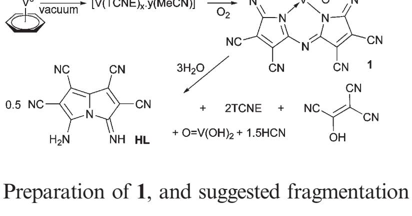


Fig. 1 UV–visible spectra (acetonitrile, 10^{-5} M) of (a) **1** (A) and its fragmentation product (B), and (b) **2**.

Thus, we suppose that a novel TCNE based macrocyclic structure, vanadyl octacyanoporphyrazine **1**, is formed as a result of the coordination of 4 TCNE species around VO^{2+} acting as the template (Scheme 1).

The reaction proceeds smoothly at room temperature in the presence of air and moisture. The IR spectrum of the product shows the typical skeletal stretching of the porphyrazine macrocycle at 1500 cm^{-1}, as well as pyrrole stretching vibration bands ($\nu_{C=N}$ 1645 cm^{-1}, $\nu_{C=C}$ 1560 cm^{-1}) and also ν_{VO} 990 cm^{-1}. It does not contain any C≡N stretching bands for free TCNE but a single $\nu_{C\equiv N}$ band at 2215 nm is observed. This can be related to the CN groups belonging to the TCNE fragments at the periphery of the macrocycle consistent with the Miller scale of average $\nu_{C\equiv N}$ as a function of the species charge, such absorptions being assigned to neutral TCNE-based species with the central C=C bond partially involved in π-donor interactions.[1a] Solid state ^{13}C NMR confirms the presence of C=C–CN fragments framing the macrocycle with a signal at 111.5 ppm for nitrile groups.

Elemental analysis of the purified product gives the empirical formula $\mathbf{1}\cdot C_6H_6\cdot 3H_2O$. The presence of water associated with peripheral CN groups was confirmed by the IR spectrum showing three broad strongly-overlapping bands in the 3200–3400 cm^{-1}



Scheme 1 Preparation of **1**, and suggested fragmentation reaction.

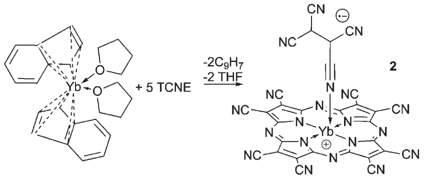
---

[a] G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinin Street 49, GSP-445, Nizhny Novgorod, 603600, Russia. E-mail: klarisa@iomc.ras.ru; Fax: +7 8132 661497; Tel: +7 8132 664370
[b] Labo. CMOS, CNRS UMR 5253, Institut Gerhardt, Université Montpellier II, Place E. Bataillon, 34095 Montpellier cedex 5, France. E-mail: douglas@univ-montp2.fr; Fax: +33 467143852; Tel: +33 467143848
[c] B. I. Stepanov Institute of Physics, National Academy of Science of Belarus, F. Skaryna Ave. 68, 220072 Minsk, Belarus. E-mail: bushuk@dragon.bas-net.by; Fax: +375 17 284 08 79; Tel: +375 17 284 04 36

† Electronic supplementary information (ESI) available: Preparation of **1** and **2**. See DOI: 10.1039/b701994g

region. However, it cannot be excluded that one of these bands results from a small number of NH groups formed from CN group hydrolysis under mild conditions in the presence of water.[1,4] The presence of C_6H_6 was confirmed by the solid state ^{13}C NMR spectrum showing a signal at 128.3 ppm typical of aromatic carbons. The association of octacyanoporphyrazine with benzene and water is rather strong. Even under MALDI ionization conditions (1,8,9-anthracenetriol matrix) the mass spectrum displayed an isotopic cluster at m/z = 711 (rel. intens. 10), corresponding to $[M^+]$, where M = $\mathbf{1}\cdot C_6H_6\cdot 3H_2O$. The most intense isotopic cluster peak is observed at m/z = 646 corresponding to demetalated and doubly protonated $[M + 2H - VO^{2+}]^+$ (rel. intens. 100). Under FAB^- ionization conditions (NBA matrix) only a peak at m/z = 531 is observed corresponding to the monoprotonated and monohydrated anionic species $[M - VO - C_6H_6 + H - 2H_2O]^-$.

This new approach to template synthesis of porphyrazines from TCNE as the structural unit was also applied to the rare earth metal π-complex $[(C_9H_7)_2Yb(THF)_2]$ resulting in the formation of the ytterbium(III) octacyanoporphyrazine complex **2** (Scheme 2) similar to that obtained in the case of the vanadium bis(arene) π-complex. The reaction of bis(indenyl)ytterbium(II)[5] with TCNE proceeds at room temperature in dry THF under vacuum and is accompanied by the destruction of the ytterbium π-complex and the formation of a green–black solid. The reaction product, only partially soluble in THF, was extracted from the reaction mixture with dry acetonitrile. The resulting deep green acetonitrile solution was evaporated to dryness under vacuum affording a dark green solid which was washed with dry toluene analogously to the procedure applied in the case of the vanadyl complex (ESI). As in the case of **1**, the IR spectrum of the ytterbium complex shows skeletal (*ca.* 1470 cm^{-1}) and pyrrole stretching vibration bands ($\nu_{C=N}$ 1638 cm^{-1}, $\nu_{C=C}$ 1563 cm^{-1}) and also a $\nu_{C\equiv N}$ s band at 2210 cm^{-1}. The UV–visible electronic absorption spectrum of the purified product (Fig. 1b(A)) is also quite similar to that for the vanadium complex, having a distinct Q-band at 680 nm ($\log \varepsilon = 4.2$) significantly broadened due to the vibrational fine structure and a Soret band at 360 nm ($\log \varepsilon = 4.0$). The absorption band at 975 nm in the near IR region (Fig. 1b(B)) is attributed to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} formed from Yb^{2+} oxidation by TCNE. Overlapping bands in the 400–500 nm region are also observed which can be attributed to the TCNE radical-anion (415 nm) and to the charge-transfer transitions Yb → octacyanoporphyrazine and/or Yb → $TCNE^{\bullet -}$.[6] This observation is consistent with the IR spectrum of the purified ytterbium complex showing additional C≡N stretch bands at 2144 cm^{-1}. According to the Miller scale of average $\nu_{C\equiv N}$ as a function of the species charge this frequency can be attributed to reduced TCNE ($TCNE^{\bullet -}$).[1,11] Although the band at 2144 cm^{-1} is not noticeably shifted towards the value for free $TCNE^{\bullet -}$ it is greatly broadened (half-width at half-height *ca.* 60 cm^{-1} *cf.* *ca.* 2 cm^{-1} for free $TCNE^{\bullet -}$) consistent with the TCNE radical-anion being bound to ytterbium in the axial position.[7] The presence of the broad unresolved signal (g = 2.0028) in the ESR spectra of the ytterbium complex recorded in both the solid state and THF solution also provides evidence for the presence of the TCNE radical-anion.



Scheme 2 Preparation of **2**.

Elemental analysis of the purified product treated with toluene showed the empirical formula $\mathbf{2}\cdot 4CH_3C_6H_5\cdot 2.5THF$. The MALDI spectrum displayed an isotopic cluster at m/z = 628.5 (z = 2), corresponding to $[M - TCNE]^{2+}$ (m = 1257) where M = $\mathbf{2}\cdot 4CH_3C_6H_5\cdot 3THF$. Curiously, the TCNE peripheral fragments in both the vanadyl and ytterbium complexes preserve, at least partly, their π-acceptor properties as shown by their bonding to aromatic molecules.

It should be noted that, previously, a similar template process affording cyano-substituted porphyrazine formation has been observed only for tricyanoethylenes.[8] However, very severe conditions were required (3–4 hours at $T > 200$ °C) and the yields were very low. It appears that the only previous mention of octacyanoporphyrazine is that in a paper on the theoretical calculations of substituent effects in porphyrazines and phthalocyanines accompanied by the remark that this particular porphyrazine has yet to be synthesized.[9] Thus, to our knowledge, we report here the first preparation of a highly functionalized porphyrazine macrocycle having 8 peripheral CN groups directly bonded to the pyrrole rings.

Both complexes are stable in air in the solid state but the vanadyl complex undergoes rapid transformation in very dilute solutions. A colour change from dark-green to violet takes place within 1–3 h accompanied by intrinsic changes in the visible spectrum. The degradation of the Soret and Q-bands takes place and the formation of a new violet dye with an absorption at 580 nm is observed (Fig. 1a(B)). Moreover, the violet solution shows a bright luminescence at 620 nm ($\lambda_{reg.}$ = 578 nm) which is not observed in the starting green solution (Fig. 2a(A)). Similar visible spectra have been observed for the pyrrolizine (**HL**) (Scheme 1) and other derivatives synthesized and investigated in detail by Flamini *et al.*[10a,b,c] Thus, these compounds may be formed as a result of porphyrazine macrocycle fragmentation with HCN elimination (Scheme 1), **HL** taking part in the associated equilibria described previously.[10d]

Size exclusion chromatography (SEC) of a dilute THF solution of **1** showed three peaks corresponding to components with molecular weights *ca.* 650, 250 and 100–150 (Fig. 2b). The first component can be obviously attributed to the porphyrazine complex. LC analysis of the same mixture in acetonitrile solution showed the presence of TCNE and tricyanoethenol readily formed from TCNE in the presence of moisture.[1a] The component with

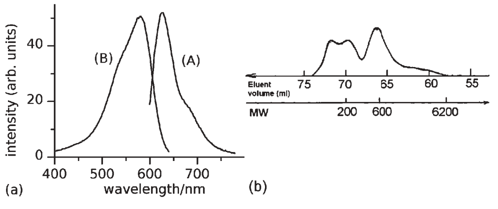


Fig. 2 Fragmentation product of **1**: (a) luminescent (A) and excitation (B) spectra in acetonitrile, and (b) SEC trace.

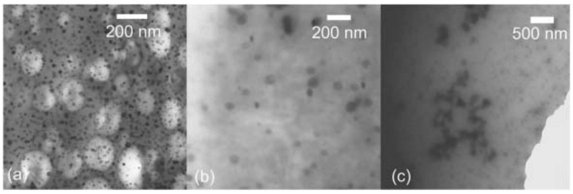


Fig. 3 TEM micrographs of films of (a) **2** cast from MeCN solution, (b) **2** in polyethylcyanoacrylate matrix, and (c) **1** in **PEAES** matrix.

molecular weight *ca.* 250 can be attributed to **HL** resulting from macrocycle fragmentation.

Both the vanadyl and the ytterbium complexes can be readily incorporated into a matrix of polymers carrying donor and/or acceptor groups. Thus, we prepared good optical-quality polymeric film-producing nanocomposites based on the metal complexes in a matrix of carbazole-containing polymers, polyvinylcarbazole, and the previously described[11] conjugated poly[(ethynylene)(arylene)(ethynylene)(silylene)] (**PEAES**) –[–C≡C–SiPh$_2$–C≡C–Ar–]– where Ar = (9*H*-carbazol-9-ylcarbonyl)-1,4-phenylene. Both complexes have also been incorporated into a matrix of the biodegradable polymer polyethylcyanoacrylate which can be used for physiologically active nanoparticle encapsulation.[12] The latter is of particular interest since the octacyanoporphyrazine framework is a chromophore showing intense absorptions in the biologically relevant window 650–800 nm. Transmission electronic microscopy (TEM) of thin films prepared from such polymeric compositions shows the presence of metal complex nanoparticles (Fig. 3).

The photoluminescence of porphyrazines and their complexes in the near IR region has been reported recently.[13] The steady-state fluorescence emission and excitation spectra of **2** incorporated into **PEAES** films‡ have been investigated. Excitation at 450 nm (corresponding to the band of the CT transition) gives a very wide emission band in the region 750–1000 nm (Fig. 4a(A)), there being no emission band in this region for **PEAES** alone (main emission band at 400 nm). Furthermore, a sharp luminescence peak at 977 nm on the edge of the main broad peak is observed. It evidently can be attributed to narrow-bandwidth emission derived from the Yb $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition (Fig. 1b(B)).[14] This transition was activated by non-direct excitation of the Yb^{3+} ion resulting from energy transfer from the ligand environment excited levels to a metal emitting level ("antenna" type excitation). The luminescence excitation spectrum at registration wavelength 780 nm shows that both $\pi \rightarrow \pi^*$ and CT transitions can be involved in such energy transfers (Fig. 4a(B)). Excitation into the Q-band maximum (680 nm) produces significantly more narrow-bandwidth emission at 880 nm (Fig. 4b(A)). Only one intense band $\lambda_{max} \sim 680$ nm is observed in the excitation spectrum at λ_{reg} 880 nm (Fig. 4b(B)) corresponding precisely to the Q-band in the absorption spectrum of **2**. Hence, luminescence arises from the first singlet macrocycle excited state (S$_1$) decaying back to the ground singlet state (S$_0$).[15]

In conclusion, the novel TCNE-based highly functionalized octacyanoporphyrazine framework, incorporated in the form of its metal complex **1** or **2** nanoparticles into polymeric matrices, exhibits interesting optical properties which make the materials most promising for various applications in electroluminescent and photovoltaic devices. Also, possibly, they may be important in biochemical applications as photosensitizers for photodynamic antitumour therapy and for medical diagnostics.

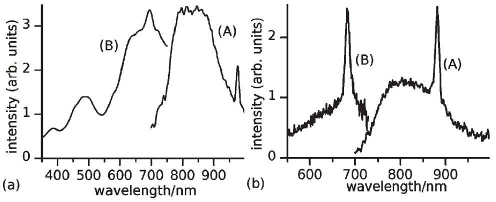


Fig. 4 Spectra of film of **2** in **PEAES** matrix:‡ (a) luminescence ($\lambda_{excitation}$ = 450 nm) (A) and excitation ($\lambda_{registration}$ = 780 nm) (B), and (b) luminescence ($\lambda_{excitation}$ = 680 nm) (A) and excitation ($\lambda_{registration}$ = 880 nm) (B).

Financial support was received from the Russian Foundation, the RAS Nanotechnology Programme, RF President Grant No. 8017.2006.3 and INTAS (Open Call Project 03-51-5959).

Notes and references

‡ Films (thickness 10 μm) containing 20 mass% of **2** incorporated into a **PEAES** matrix were prepared by spin-coating from THF solution.

1 (*a*) J. S. Miller, *Angew. Chem., Int. Ed.*, 2006, **45**, 2508–2525; (*b*) D. C. Gordon, L. Deakin, A. M. Arif and J. S. Miller, *J. Am. Chem. Soc.*, 2000, **122**, 290–299; (*c*) J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385–415; (*d*) J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein and J. S. Miller, *Science*, 1991, **252**, 1415–1417.

2 E. Pretsch, W. Simon, J. Seibl and T. Clerc, *Table of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin-Heidelberg, 1989, p. 1190.

3 L. Edwards and M. Gouterman, *J. Mol. Spectrosc.*, 1970, **33**, 292–310.

4 F. Conan, B. Le Gall, J.-M. Kerbaol, S. Le Stang, J. Sala-Pala, Y. Le Mest, J. Bacsa, X. Ouyang, K. R. Dunbar and C. F. Campana, *Inorg. Chem.*, 2004, **43**, 3673–3681.

5 A. A. Trifonov, E. A. Fedorova, V. N. Ikorskii, S. Dechert, H. Schumann and M. N. Bochkarev, *Eur. J. Inorg. Chem.*, 2005, 2812–2818.

6 M. J. Stillman and T. Nyokong, in *Phthalocyanines – Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, vol. 1, ch. 3, p. 131; C. N. R. Rao, S. N. Bhat and P. C. Dwivedi, *Appl. Spectrosc. Rev.*, 1971, **5**, 1–170.

7 D. A. Summerville, T. W. Cape, E. D. Johnson and F. Basolo, *Inorg. Chem.*, 1978, **17**, 3297–3300.

8 V. N. Kopranenkov, L. S. Gorcharova and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1979, **49**, 1408–1412.

9 A. Ghosh, P. G. Gassman and J. Almloef, *J. Am. Chem. Soc.*, 1994, **116**, 1932–1940.

10 (*a*) A. Flamini, *Curr. Org. Chem.*, 2003, **7**, 1793–1820; (*b*) A. Panusa, A. Flamini and N. Poli, *Chem. Mater.*, 1996, **8**, 1202–1209; (*c*) A. Flamini, P. Ghalsasi, T. D. Selby and J. L. Miller, *Inorg. Synth.*, 2004, **34**, 68–76; (*d*) E. Collange, A. Flamini and R. Poli, *J. Phys. Chem. A*, 2002, **106**, 200–208.

11 W. E. Douglas, R. E. Benfield, O. L. Antipov, L. G. Klapshina, A. S. Kuzhelev, D. M. H. Guy, R. G. Jones, A. Mustafa and G. A. Domrachev, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3195–3201.

12 H. Boudad, P. Legrand, G. Lebas, M. Cheron, D. Duchene and G. Ponchel, *Int. J. Pharm.*, 2001, **218**, 113–124.

13 B. J. Vesper, S. Lee, N. D. Hammer, K. M. Elseth, A. G. M. Barrett, B. M. Hoffman and J. A. Radosevich, *J. Photochem. Photobiol., B*, 2006, **82**, 180–186.

14 B. S. Harrison, T. J. Foley, M. Bouguettaya, J. M. Boncella, J. R. Reynolds, K. S. Schanze, J. Shim, P. H. Holloway, G. Padmanaban and S. Ramakrishnan, *Appl. Phys. Lett.*, 2001, **79**, 3770–3772.

15 R. Paolesse, A. Marini, S. Nardis, A. Froiio, F. Mandoj, D. J. Nurco, L. Prodi, M. Montalti and K. M. Smith, *J. Porphyrins Phthalocyanines*, 2003, **7**, 25–36.