PAPER www.rsc.org/njc | New Journal of Chemistry

N-Carbazolylmethylphosphonic acid—synthesis, metal coordination, emissive aggregate formation and spectroscopic features†

Ester Buchaca, Siud Pui Man, Majid Motevalli, John Wilson and Alice Sullivan*

Received (in Victoria, Australia) 6th April 2010, Accepted 7th June 2010
DOI: 10.1039/c0nj00260g

The synthesis and characterisation of *N*-carbazolylmethylphosphonic acid **1**, the spectrophotometric absorption and emission features of aqueous **1** and its di-sodium phosphonate derivative **2** and the absorption and fluorescence response of micromolar **2** to divalent metals zinc, copper, calcium and manganese are described. A manganese derivative **3** was formed in the reaction between **1** and manganese carbonate and the structure of **3** elucidated by single crystal X-ray diffraction and displaying stacked carbazole units is presented. Atomic force microscopy (AFM) and fluorescence microscopy images show that spin coating may be used to deposit blue emitting micron sized assemblies of **1** on glass substrates from micromolar chloroform solutions of **1**.

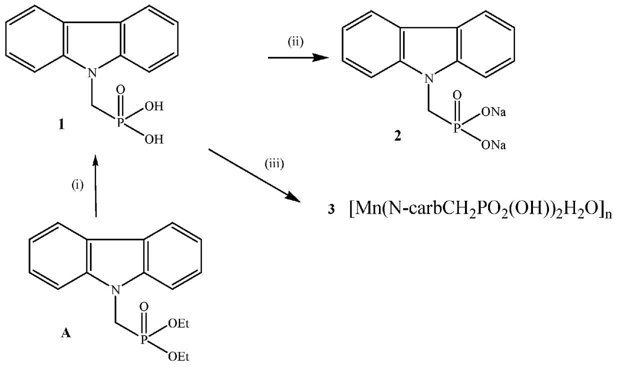
Introduction

The phosphonate group –$PO(OR)_2$ offers a diverse range of metal binding possibilities depending on its constitution as diester or the mono or dianion. While there are many structurally characterised metal phosphonates known, examples where the phosphonate contains a fluorescent organic group are rare. We are studying the interactions between metals and new ligands with phosphonate groups –$PO(OR)_2$ attached to organic fluorescent moieties. The effect of these interactions on the intrinsic fluorescence properties of the fluor is important regarding the potential applications of these compounds that exploit their emissive properties. Recent reviews on phosphonate chemistry indicate that the range of interests driving this field cover catalysis, magnetochemistry, photochemistry, materials chemistry and biological applications.[1] We previously reported on quinolinyloxymethylphosphonates in the context of fluorescent sensing of metal ions.[2] Carbazole and its derivatives have been incorporated in a range of materials to support properties and applications such as electroluminescence,[3] photoconductivity[4] and non-linear optical effects.[5] Moreover its photophysical properties have allowed it to be developed as a sensor for anions.[6] The carbazole group is also found in the biologically active carbazole alkaloids.[7] In this paper we report on the blue emissive compound *N*-carbazolylmethylphosphonic acid **1** and the spectrophotometric response (absorption and emission) of aqueous **1** to aqueous Na^+, Ca^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}. Single crystals of the manganese(II) derivative **3** were isolated and the X-ray structure provides an example of the interesting type of solid state assembly adopted by this system. We also found that blue emitting micron sized aggregates of **1** can be deposited from its micromolar solutions.

Results and discussion

Synthesis

The *N*-carbazole methylphosphonic acid compound **1** (Scheme 1) was obtained by hydrolysis of the corresponding phosphonate ester **A**[8] mediated by trimethylsilyl iodide. A single peak was seen in the proton-decoupled ^{31}P spectrum of **1** at δ_P 17.17 considerably upfield from that observed for the parent diester. The composition of **1** was confirmed by elemental analysis and mass spectroscopy. Solutions of the disodium phosphonate **2** were prepared upon addition of 2 equivalents of NaOH to solutions of **1** and these were subsequently titrated with a range of metal nitrates using emission spectroscopy to follow the fluorescence response. To demonstrate the coordination behaviour of **1**, we attempted to form complexes by a number of different routes using different metal compounds. In the event single crystals of a manganese derivative **3** were formed as fine almost colourless needles when compound **1** and manganese carbonate were mixed in methanol and water and held at 120 °C following a protocol adapted from Lin *et al.*[9] The crystalline material was seen for 1 : 2 but not 1 : 1



Scheme 1 (i) Trimethylsilyl iodide, methanol. (ii) Aqueous sodium hydroxide. (iii) Manganese carbonate in methanol–water 120 °C gives $[Mn(N\text{-carbCH}_2PO_2(OH))_2\cdot H_2O]_n$ **3**.

School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, UK.
E-mail: a.c.sullivan@qmul.ac.uk

† CCDC reference numbers 779813. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00260g

stoichiometric ratio of **1** : $MnCO_3$ and the needles could be separated by hand from the rest of the reaction mixture. The solid state structure of **3** is discussed below.

Structure of compound 3. There was difficulty in obtaining high quality crystals of **3** for data collection. Several crystals from different batches were investigated and the data presented here represent the best obtained. Data analysis ruled out the possibility of a non-centrosymmetric space group and $P2_1/c$ was thus confirmed. In order to improve the quality of the fit to these data, reflections showing low resolution were excluded. All the P–(OH) hydrogens and the hydrogens of the coordinated water molecule were located on the difference map.

The solid-state structure of compound **3** is shown in Fig. 1, selected bond distances and angles in Table 1 and crystal data are given in the Experimental section. The simplest representation of the structural unit consists of the dinuclear species shown in Fig. 1. It can be seen from the bond angles in Table 1 that the geometry at manganese is essentially octahedral and the extended structure may be viewed as a series of edge-shared MnO_6 bi-octahedra connected by *N*-carb-CH_2P groups as shown in Fig. 2. The six ligating moieties comprise four PO–Mn bonds, two where the donor oxygen is μ_2-bridging and two where the donor oxygen is μ_3-bridging between phosphorus and two manganese atoms. The fifth and sixth positions are filled by a PO(H)Mn bond and a coordinated water molecule. Thus there are two types of *N*-carb$CH_2PO_2(OH)$ groups in the structure, one involved in linking the edge-shared bi-octahedra and the other, a monodentate phosphonate ligand, occupies an apical position. It is not possible to be certain which of the donor oxygens μ_2-POMn or μ_3-PO$(Mn)_2$ is a phosphonyl P=O–Mn or phosphonate P–O–Mn although the μ_3-POMn has the shorter P–O bond distance. It is noteworthy that in the case of monodentate *N*-carb$CH_2PO_2(OH)$ the coordinated P–O(7) distance is shorter (1.491(5) Å) than uncoordinated and likely phosphonyl P–O(5) (1.527(5) Å). An empirical formula describing the system is $[Mn(N\text{-carb}CH_2PO_2(OH))_2\cdot H_2O]$. Fig. 3 shows how the structure builds up in three dimensions along the *y*-direction to give

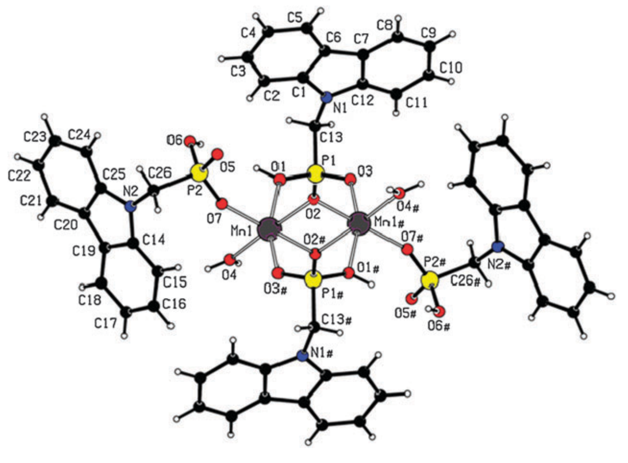


Fig. 1 Compound **3** showing the manganese coordination sphere. Symmetry code: # $-x + 1, -y + 1, -z + 1$.

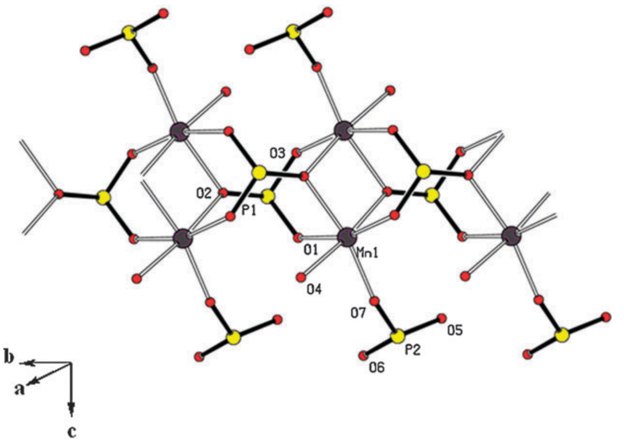


Fig. 2 Compound **3** showing phosphonate interconnected 8-rings.

Table 1 Selected bond distances (Å) and angles (°) for **3**

Mn(1)–O(7)	2.058(5)	O(7)–Mn(1)–O(3)	101.0(2)	P(1)–O(2)–Mn(1)#1	136.4(3)
Mn(1)–O(3)	2.162(5)	O(7)–Mn(1)–O(4)	84.1(2)	P(1)–O(2)–Mn(1)#4	129.8(3)
Mn(1)–O(4)	2.176(6)	O(3)–Mn(1)–O(4)	97.4(2)	Mn(1)#1–O(2)–Mn(1)#4	93.43(18)
Mn(1)–O(2)#1	2.185(5)	O(7)–Mn(1)–O(2)#1	101.1(2)	P(1)–O(3)–Mn(1)	126.5(3)
Mn(1)–O(2)#2	2.201(5)	O(3)–Mn(1)–O(2)#1	85.00(19)	Mn(1)–O(4)–H(41W)	112(5)
Mn(1)–O(1)#3	2.351(5)	O(4)–Mn(1)–O(2)#1	173.7(2)	Mn(1)–O(4)–H(42W)	134(7)
Mn(1)–Mn(1)#3	3.193(2)	O(7)–Mn(1)–O(2)#2	167.9(2)	H(41W)–O(4)–H(42W)	114(7)
O(1)–P(1)	1.573(5)	O(3)–Mn(1)–O(2)#2	88.90(18)	P(2)–O(6)–H(61)	115(8)
O(1)–Mn(1)#3	2.351(5)	O(4)–Mn(1)–O(2)#2	87.7(2)	P(2)–O(7)–Mn(1)	156.4(3)
O(1)–H(71)	0.94(5)	O(2)#1–Mn(1)–O(2)#2	86.57(19)	O(3)–P(1)–O(2)	114.3(3)
O(2)–P(1)	1.526(5)	O(7)–Mn(1)–O(1)#3	92.0(2)	O(3)–P(1)–O(1)	108.7(3)
O(2)–Mn(1)#1	2.185(5)	O(3)–Mn(1)–O(1)#3	162.55(18)	O(2)–P(1)–O(1)	110.3(3)
O(2)–Mn(1)#4	2.201(5)	O(4)–Mn(1)–O(1)#3	95.4(2)	O(3)–P(1)–C(13)	109.3(3)
O(3)–P(1)	1.510(5)	O(2)#1–Mn(1)–O(1)#3	81.10(19)	O(2)–P(1)–C(13)	106.2(3)
O(4)–H(41W)	0.86(4)	O(2)#2–Mn(1)–O(1)#3	79.82(18)	O(1)–P(1)–C(13)	107.9(3)
O(4)–H(42W)	0.85(5)	P(1)–O(1)–Mn(1)#3	126.9(3)	O(7)–P(2)–O(5)	114.0(3)
O(5)–P(2)	1.527(5)	P(1)–O(1)–H(71)	120(5)	O(7)–P(2)–O(6)	110.7(3)
O(6)–P(2)	1.558(5)	Mn(1)#3–O(1)–H(71)	110(5)	O(5)–P(2)–O(6)	109.8(3)
O(6)–H(61)	0.90(5)			O(7)–P(2)–C(26)	110.8(4)
O(7)–P(2)	1.491(5)			O(5)–P(2)–C(26)	105.4(3)
				O(6)–P(2)–C(26)	105.7(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z + 1$ #2 $x, y - 1, z$ #3 $-x + 1, -y + 1, -z + 1$ #4 $x, y + 1, z$.

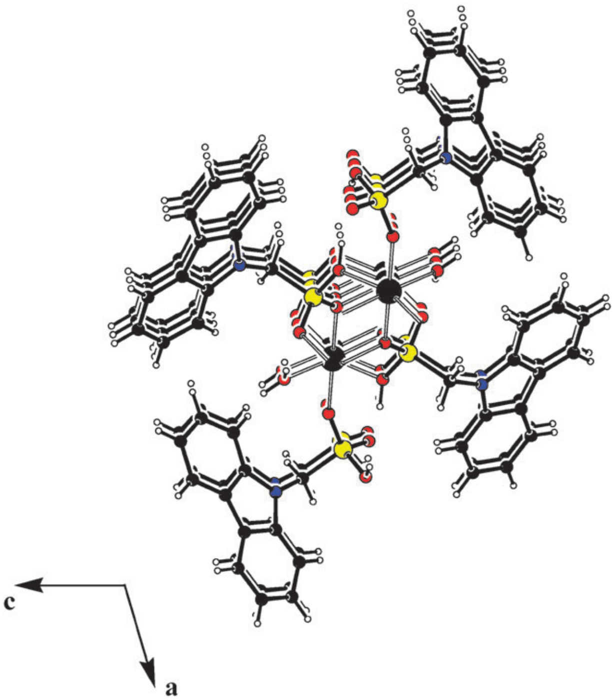


Fig. 3 Compound **3** showing a view of stacked carbazole groups (down the *y*-axis) around the inorganic core.

columns consisting of a metal oxide core surrounded by outer face-to-face stacks of *N*-carbazole groups. The carbazole C_6-ring centroid-to-centroid distance for a pair of neighbouring rings was found to be 4.753 Å which is greater than the van der Waals distance so typical van der Waals interactions between these rings seem unlikely.[10]

The key bond distances Mn–O(P) in **3** are in agreement with similar distances in $Mn[HO_3PCH_2C_6H_4COOH]_2{\cdot}2H_2O$.[11]

Spectrophotometric features of 1 and 2. The pair of π–π* transitions at 261 and 294 nm in **1** are red shifted by 2 and 4 nm, respectively, compared to the parent phosphonate ester and carbazole while the n–π* bands at 332 and 348 nm are shifted more than 10 nm (Fig. 4).

Compound **1** is moderately emissive, the quantum yield Φ_1 0.30 was determined for **1** using anthracene as a reference.[12] The observed emission bands for **1** have a similar shape to those of the parent ester and carbazole[13] but are red shifted by 11 nm (Fig. 4). This is of similar magnitude to the shift seen for n–π* absorption bands.

Addition of up to 2 equivalents NaOH to dilute aqueous **1** was accompanied by a shift of the π–π* absorption bands at 290 to 293 nm and 262 to 260 nm coinciding with isosbestic points at 278 and 293 nm (Fig. 5). The n–π* bands at 331 and 345 nm are also shifted slightly resulting in isosbestic points at 335, 341 and 348 nm. A pK_1 value of 2.14 for the more acidic P–OH was evaluated using fractional composition *versus* pH analysis and absorbance changes at 292 and 294 nm either side of the isosbestic at 293 nm. Phosphonic acids $RPO(OH)_2$ typically have $pK_1 \approx 2$. In the corresponding deprotonation

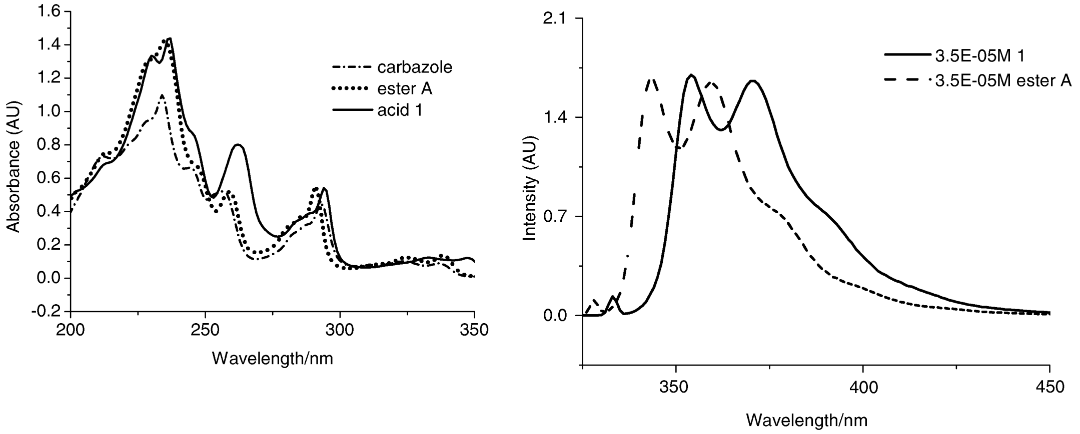


Fig. 4 Comparison of absorption (left) and emission (right) of **1** *vs.* parent phosphonate ester in ethanol, λ_{ex} 333 nm.

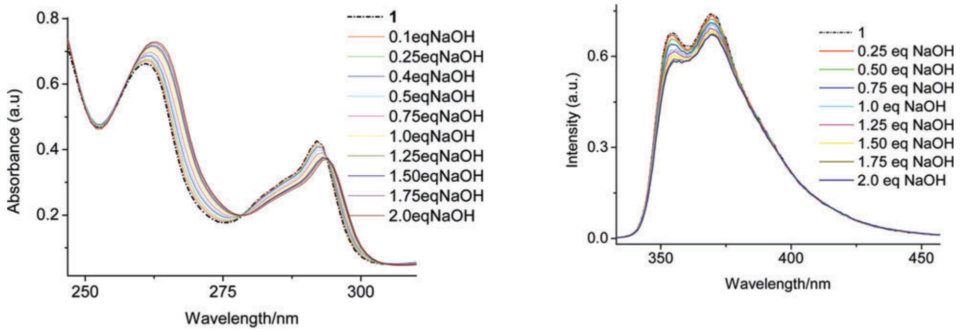


Fig. 5 Absorption (left) and emission (right) for deprotonation titration of 35 μM and 5 μM aqueous **1** with 10 mM NaOH (λ_{ex} 292 nm).

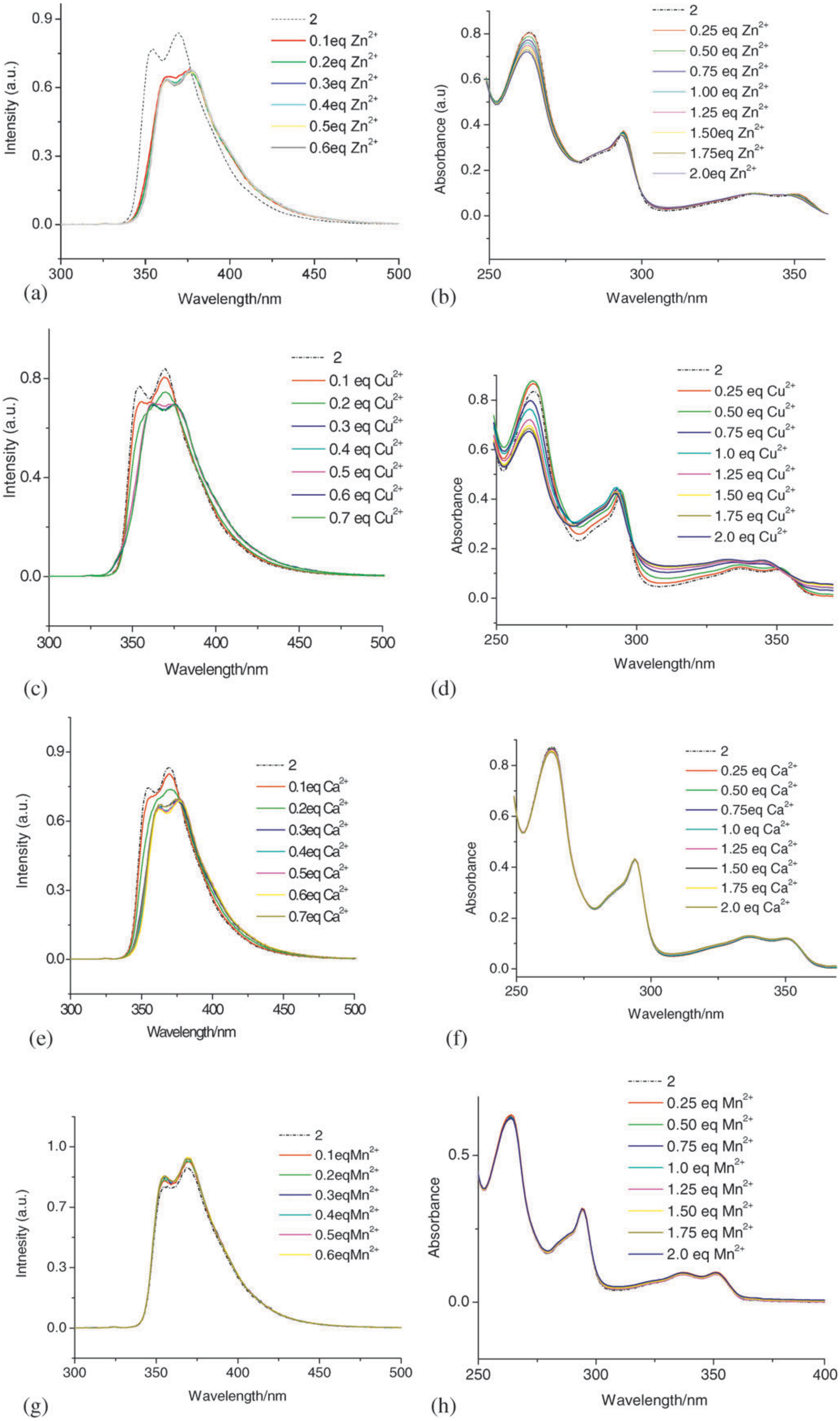


Fig. 6 Emission (left) and absorption (right) spectra for titration of 5 μM and 35 μM aqueous **2** with (a) and (b) Zn^{2+}, (c) and (d) Cu^{2+}, (e) and (f) Ca^{2+}, (g) and (h) Mn^{2+}, λ_{ex} 293 nm.

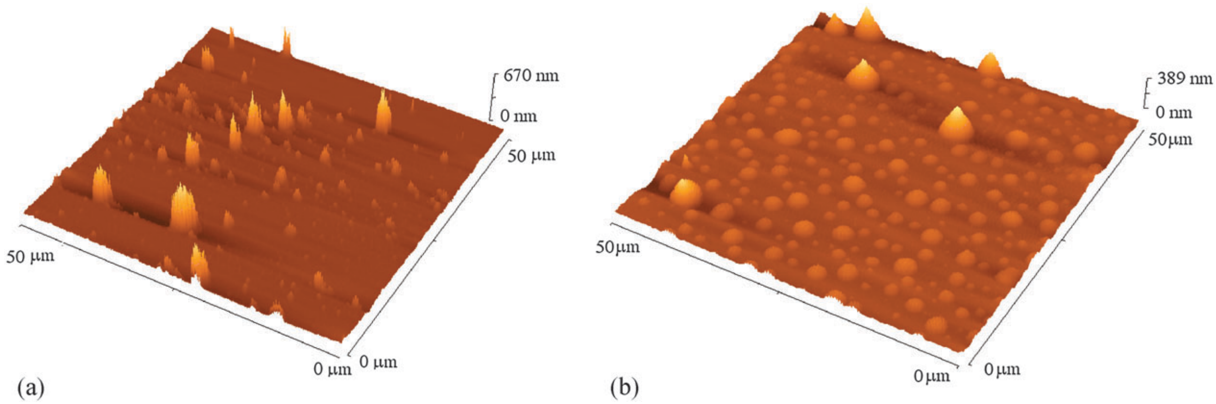


Fig. 7 Atomic force microscopy images: (a) non-coated glass; (b) spin-coated glass (100 µL, 0.3 µM **1**, in $CHCl_3$), dried at 80 °C.

experiment using fluorescence, the emission of 5 µM **1** is slightly quenched but not shifted (Fig. 5) after the addition of 2 equivalents of NaOH to give solutions **2** of sodium phosphonate.

We subsequently measured the fluorescence and absorption response of 5 µM and 35 µM **2**, respectively, to titration with the biologically important metals Zn^{2+}, Cu^{2+}, Ca^{2+} and Mn^{2+} (Fig. 6) to see if there was any discrimination. The emission was slightly quenched and red shifted 8–9 nm when aqueous **2** was titrated with the aqueous metal nitrates of Zn^{2+}, Cu^{2+} and Ca^{2+} but showed very little change when titrated with Mn^{2+}. An emission shift response like this is indicative of metal cation induced charge separated excited states. For Zn^{2+} the shift was complete after addition of only 0.2 equivalents but occurred more gradually for Cu^{2+} and Ca^{2+} being complete at about 0.5 equivalents of added metal ion. This is consistent with the process involving a greater than 1 : 1 ligand to metal interaction. The Mn^{2+} aquo ion does not appear to induce an emission shift. Only in the case of Cu^{2+} is metal ion interaction with aqueous **2** evidenced by the appearance of distinct isosbestic points around the π–π* bands in the absorption spectra. These studies indicate that absorption and emission responses of dilute solutions of **2** are indeed sensitive to the nature of added divalent metal.

Emissive aggregates of 1. Phosphonic acids are known to self-associate in solution and to form monolayers on various surfaces.[14] It was thus of interest to determine whether self-assembled structures of **1** could be deposited or grown on a surface. Thus we report here on an experiment in which glass slides were spin coated from micromolar solutions of **1** in chloroform. The deposition of discrete aggregates of **1** was indicated by AFM images and fluorescence microscopy (λ_{ex} 365 nm) images of the coated glass slides. These aggregates were mostly spherical in shape and had diameters ~1–3 µm. The deposited structures were observed to be blue emitting using fluorescence microscopy (Fig. 7 and 8).

Several electroluminescent materials containing the carbazole group have been used in light emitting diode (LED) devices.[3] Our system is of interest for such applications and will be investigated further in this regard.

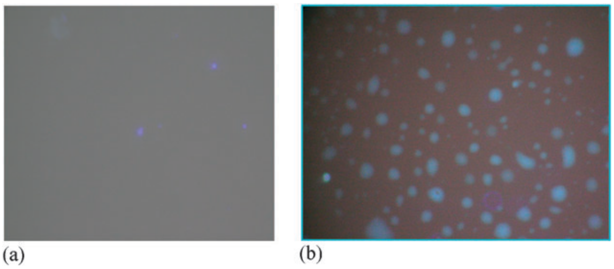


Fig. 8 Fluorescence microscopy: (a) background glass slide (b) spin-coated glass (100 µL, 0.3 µM **1**, in $CHCl_3$), dried at 80 °C.

Conclusions

N-Carbazolyloxymethylphosphonic acid **1** has been synthesised and spectroscopically characterised. In this study we found that the emission from **1** is red shifted with respect to the parent phosphonate diester and carbazole but only slightly quenched in the presence of 2 equivalents of sodium hydroxide. The fluorescence response of the aqueous micromolar solutions to various metal nitrates in water was indicative of metal cation induced charge separated excited states for Zn^{2+}, Cu^{2+} and Ca^{2+} aquo ions. A significant absorption response was seen only in the case of Cu^{2+} aquo ion. It is possible that hydrogen bonded aggregates of the phosphonic acid exist in these micromolar solutions facilitating interactions between emitting sites. Indeed spherical micron size particles of aggregated **1** could be spin coated on glass from micromolar **1**. Structural characterisation of a manganese(II) derivative **3** revealed that the emitting carbazole centers favour stacked column arrangements in the solid state although there is no direct evidence for π–π interactions.

Experimental

Solvents DMSO and DCM were dried over and distilled from molecular sieves and calcium hydride, respectively, and subsequently stored over molecular sieves.

Reagents and spectroscopic grade solvents were purchased from Aldrich, Lancaster, Fluka or Avocado and were used without further purification.

NMR spectra were recorded on: JEOL 270 (^1H, 270 MHz; ^{13}C-{^1H}, 67.9 MHz; ^{31}P{^1H}, 109.3 MHz), Bruker AM250

(^{1}H, 250 MHz; ^{13}C-{^{1}H}, 62.9 MHz) and AMX600 (^{1}H, 600 MHz; ^{13}C-{^{1}H}, 150.90 MHz; ^{31}P{^{1}H}, 242.92 MHz) spectrometers. The chemical shifts are reported in parts per million (ppm) relative to the position of the solvent signal. The chemical shifts (δ) for the solvents are $CDCl_3$ (^{1}H, 7.26, ^{13}C, 77.23), CD_3OD (^{1}H, 4.87, ^{13}C, 49.15) and DMSO-d_6 (^{1}H, 2.50, ^{13}C, 39.50). A combination of one-and two-dimensional experiments involving long-range (multiple bond) ^{1}H–^{13}C correlation spectroscopy were used to confirm the NMR assignments. Infrared spectra were recorded on a SHIMADZU FTIR 8300 equipped with an ATR (Attenuated Total Reflectance) attachment in the range of 4000–400 cm^{-1}. Mass spectra were obtained from services at the School of Pharmacy, London, and the EPSRC Mass Spectrometry service at the University of Swansea.

Elemental analyses (carbon, hydrogen, nitrogen) were obtained from services at University College London. Melting points were observed on an electrothermal melting point apparatus.

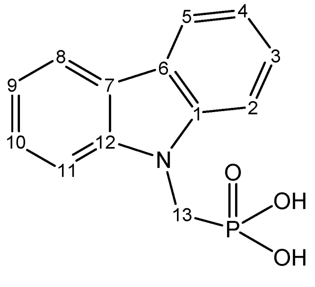
UV-vis spectra were recorded on a Hewlett-Packard 845× UV–visible system equipped with a deuterium and tungsten lamp with 1 cm quartz cells at room temperature.

Fluorescence spectra were obtained from a Yvon Jobin Fluoromax 3 instrument. Stock solutions of **1** 0.005 M in ethanol were diluted in water. Solutions of **2** were prepared by addition of 2 equiv. of NaOH to **1** and diluted as required. Aqueous 5 μM **1** and **2** contained 0.1% ethanol while aqueous 35 μM **1** and **2** contained 0.7% ethanol.

The spectrophotometric titrations (uncorrected for performance of the instrument) were performed by addition of metal ion solutions (0.001 M) in 1.5 μL aliquots to 3 mL of 5 μM **1**. The change in concentration of **1** was assumed to be negligible.

Preparation of *N*-carbazolylmethylphosphonic acid 1

To a stirred solution of diethyl-*N*-carbazolylmethylphosphonate (0.99 g, 3.12 mmol) dissolved in dry dichloromethane (10 cm^3) under an atmosphere of nitrogen was added trimethylsilyl iodide (1.8 cm^3). The red solution was stirred for 2 h then methanol (15 cm^3) was added. After a further 2 h stirring the solvent was removed under reduced pressure and water (20 cm^3) added. The mixture was then concentrated under reduced pressure. This step was repeated four times to give **1** as an off-white solid (0.65 g, 82%).



Melting point: 245–247 °C.

High Resolution Mass Spec. Found: 279.089, $C_{13}H_{16}N_2O_3P$ $[M + NH_4]^+$ requires 279.089.

Found: C 55.62; H 4.50; N 4.85%. Calculated for **1**·H_2O $C_{13}H_{14}NO_4P$: C 55.92; H 5.05; N 5.02%.

^{1}H (270 MHz, DMSO-d_6) 8.12 (2H, d, J 7.4 Hz, H_5 and H_8), 7.58 (2H, d, J 8 Hz, H_2 and H_{11}), 7.42 (2H, dd, J_1 8 Hz, J_2 7.4 Hz, H_4 and H_9), 7.18 (2H, dd, J_1 8 Hz, J_2 7.4 Hz, H_3 and H_{10}) and 4.59 (2H, d, J 9.4 Hz, H_{13}).

^{31}P-{^{1}H} (109.3 MHz, DMSO-d_6) +17.17.

IR (ν_{max}/cm^{-1}) 3439br (O–H), 2882br ((P)O–H), 1601w ($Ar_{C=C}$), 1488m ($Ar_{C=C}$), 1454m, 1415w, 1323w (C–N), 1261w (P=O), 1110m, 1026s, 964s, 744s, 717s, 505s, 486w, 451s, 413w.

Following the Jobin Yvon Horiba method using anthracene as standard sample, the quantum yield of **1** was determined $\Phi_F = 0.3$.[12]

Preparation of compound 3

In a heavy-walled Pyrex tube, a mixture of $MnCO_3$ (0.022 g, 0.2 mmol) and **1** (0.026 g, 0.1 mmol) was thoroughly mixed in methanol (1.0 mL) and H_2O (0.2 mL). The tube was frozen, sealed under vacuum and then placed in an oven at 120 °C. After 48 h almost colorless needles were visible along with fine powder and a quantity of these crystals were separated (0.010 g, 33%). Several of the crystals selected from this batch were shown to have the same unit cell and data were collected on the best of these.

Melting point: decomposed above 340 °C

IR (cm^{-1}) 3422br (OH), 1601w (OH), 1489m ($Ar_{C=C}$), 1458s, 1419m, 1326w (C–N), 1257 m (P=O), 1157m, 1033m, 948m, 748s, 721m, 529m, 486w.

Note: no needle like crystals were observed when a 1 : 1 mole ratio of $MnCO_3$ and **1** was employed.

X-Ray crystallography on 3

A colourless needle with approximate dimensions of 0.26 × 0.04 × 0.01 mm was chosen for diffraction study. Data were collected at 120 K using a Nonius Kappa CCD area detector diffractometer mounted at the window of a molybdenum rotating anode (50 KV, 85 mA, $\lambda = 0.71073$ Å). The crystal-to-detector distance was 30 mm and ϕ and Ω scans (1.0° increments, 20 s exposure time) were carried out to fill the Ewald sphere.

Data collection and processing were carried out using DirAx,[15] COLLECT,[16] DENZO[17] and an empirical absorption correction was applied using SADABS.[18]

The structure was solved by the direct method using the SHELXS-97[19] program, refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2 using the SHELXL-97 program.[19] The programs ORTEP-3[20] and PLATON[21] were used for drawing the molecules. WINGX[22] was used to prepare material for publication.

Crystal data and refinement details are given below.

Compound 3

$C_{26}H_{24}MnN_2O_7P_2$, $M = 593.35$, monoclinic, $a = 18.373(2)$, $b = 4.7525(4)$, $c = 29.191(3)$ Å, $\beta = 107.101(3)°$, $V = 2436.2(4)$ Å^3, space group $P2_1/c$, Mo-Kα ($\lambda = 0.71073$ Å), $Z = 4$, $D_c = 1.618$ Mg m^{-3}, $\mu = 0.726$ mm^{-1}, reflections measured 18 437, reflections unique 3445 with $R_{int} = 0.1148$, $T = 120(2)$ K, final R indices {$I > 2\sigma(I)$} $R_1 = 0.0861$, w$R_2 = 0.1498$, and for all data $R_1 = 0.1167$, w$R_2 = 0.1610$.†

Acknowledgements

We thank Dr H. Toms and Mr Greg Coumbarides for NMR spectra, the EPSRC Mass Spectroscopy Service at Swansea for HRMS, EPSRC National Crystallography Service, Southampton, for data collection, Queen Mary University of London for DTA funding to EB.

References

1 (*a*) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248–1256; (*b*) M. Wang, C. Ma, H.-M. Wen and C. Chen, *Dalton Trans.*, 2009, 994–1003; (*c*) J.-G. Mao, *Coord. Chem. Rev.*, 2007, **251**, 1493–1520; (*d*) G. K. H. Shimizu, R. Vaidhyanathan and J. M. Taylor, *Chem. Soc. Rev.*, 2009, **38**, 1430–1449; (*e*) S. Shibuya and Y. Zasshi, *J. Pharm. Soc., Jpn*, 2004, **124**, 725–749.

2 S. P. Man, M. Motevalli, S. Al-Juaid, F. Esan, E. Buchaca, D. Benoit, A. C. Sullivan and J. R. H. Wilson, *Inorg. Chem.*, 2006, **45**, 5328–5337.

3 (*a*) S. Maruyama, X.-T. Tao, H. Hokari, T. Noh, Y. Zhang, T. Wada, H. Sasabe, H. Suzuki, T. Watanabe and S. Miyata, *J. Mater. Chem.*, 1999, **9**, 893; (*b*) P. Kundu, K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-H. Chien, *Adv. Funct. Mater.*, 2003, **13**, 445–452; (*c*) V. Promarak and S. Ruchirawat, *Tetrahedron*, 2007, **63**, 1602–1609; (*d*) V. Promarak, A. Pankvuanga and S. Ruchirawat, *Tetrahedron Lett.*, 2007, **48**, 1151–1154; (*e*) S. Barik and S. Valiyaveettil, *Macromolecules*, 2008, **41**, 6376–6386; (*f*) X.-J. Zhang, Y.-P. Tian, S.-L. Li, M. Jiang, A. Usman, S. Chantrapromma, H.-K. Hoong-Kun, X.-J. Fun and X.-J. Zhang, *Polyhedron*, 2003, **22**, 397–402; (*g*) N. Tian, A. Thiessen, R. Schiewek, O. J. Schmitz, D. Hertel, K. Meerholz and E. Holder, *J. Org. Chem.*, 2009, **74**, 2718–2725; (*h*) L. Akcelrud, *Prog. Polym. Sci.*, 2003, **28**, 875–962.

4 (*a*) T. Wada, Y. D. Zhang, Y. S. Choi and H. Sasabe, *J. Phys. D: Appl. Phys.*, 1993, **26**, B221; (*b*) J. V. Grazulevicius, P. Strohriegl, J. Pielichowski and K. Pielichowski, *Prog. Polym. Sci.*, 2003, **28**, 1297–1353.

5 (*a*) Q. Wang, L. Wang, H. Saadeh and L. P. Yu, *Chem. Commun.*, 1999, 1689; (*b*) P. Cheben, F. del Monte, D. J. Worsfolds, D. J. Carlsson, C. P. Grover and J. D. Mackenzie, *Nature*, 2000, **408**, 64; (*c*) Z. Kotler, J. Segal, M. Sigalov, A. Ben-Asuly and V. Khodorkovsky, *Synth. Met.*, 2000, **115**, 269–273.

6 (*a*) C. X. Jiao, C. G. Niu, S. Y. Huan, Q. Shen, Y. Yang, G. L. Shen and R. Q. Yu, *Talanta*, 2004, **64**, 637; (*b*) D. Curiel, A. Cowley and P. D. Beer, *Chem. Commun.*, 2005, 236.

7 H.-J. Knölker and K. R. Reddy, *Chem. Rev.*, 2002, **102**, 4303–4427.

8 L. Robson, J. Wilson and A. C. Sullivan, *Eur. Patent Appl.*, 1625134, 2006.

9 O. R. Evans, D. R. Manke and W. Lin, *Chem. Mater.*, 2002, **14**, 3866.

10 C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, *J. Chem. Soc., Perkin Trans. 2*, 2001, **2**, 651; C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, **21**, 3885.

11 N. Stock and T. Bein, *J. Mater. Chem.*, 2005, **15**, 1384.

12 http://www.jobinyvon.com/usadivisions/Fluorescence/applications/quantumyieldstrad.pdf.

13 S. V. Lowen, J. B. R. Mastantuono, D. A. Holden, G. J. Kovacs and R. O. Loutfy, *Macromolecules*, 1990, **23**, 3242; P. Bruck, A. Ledwith and A. C. White, *J. Chem. Soc. B*, 1970, **13**, 205.

14 (*a*) A. Brun, D. Albouy, E. Perez, I. Rico-Lattes and G. Etemad-Moghadam, *Langmuir*, 2001, **17**, 5208; (*b*) S. C. D'Andrea and A. Y. Fadeev, *Langmuir*, 2003, **19**, 7268.

15 A. J. M. Duisenberg, DirAx Indexing in Single-Crystal Diffractometry with an Obstinate List of Reflections, *J. Appl. Crystallogr.*, 1992, **25**, 92–96; A. J. M. Duisenberg, R. W. W. Hooft, A. M. M. Schreurs and J. Kroon, Accurate cells from area-detector images, *J. Appl. Crystallogr.*, 2000, **33**, 893–898.

16 R. Hooft, *COLLECT: a program for crystal data collection and processing user interface*, Nonius BV, 1998.

17 Z. Otwinowski and W. Minor, Processing of X-ray diffraction data collected in oscillation mode, *Macromol. Crystallogr., Part A.*, 1997, **276**, 307–326.

18 G. M. Sheldrick, *SADABS Version 2007/2*, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.

19 G. M. Sheldrick, SHELX, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

20 L. J. Farrugia, ORTEP3 for Windows, *J. Appl. Crystallogr.*, 1997, **30**, 565.

21 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

22 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.