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ARTICLE

Concentration dependent ratiometric turn-on selective fluorescence detection of picric acid in aqueous and non-aqueous media

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A phosphorictriamide scaffold, [(NHAQ)$_3$P=O] (TAQP), having an electron-rich aminoquinoline (AQ) chromophore is shown to exhibit a ratiometric turn-on response for picric acid (PA) in lower (1x10^{-5}M) concentration of via a proton-transfer pathway. However, due to the presence of strong H-bonding and π…π interactions at higher concentrations (1x10^{-3}M), it exhibits only a luminescence quenching behaviour for PA. These effects can be observed in both protic and non-protic systems. The detection limit for this aqueous phase turn-on sensing was found to be 0.2 ppm.

Introduction

Detection of picric acid (PA) in water bodies is an important issue in society due to the increasing demands of national security and environmental protection.[1] PA, one of the many commonly known hazardous nitro-explosives, is frequently found in soil and ground water in regions near armament facilities.[2] Despite of its higher explosive power than tri-nitrotoluene (TNT), PA is still been used in dye and leathering industries, firework and matchbox factories and in some pharmaceutical products.[3] As a result, a vast amount of PA has been released in to environment. Owing to its strongly acidic nature it causes damage to skin, eye, liver and respiratory systems and also causes a number of chronic diseases due to its slow degradation under physiological conditions.[4] Several chromatographic and spectroscopic methods have been developed for PA sensing of which fluorescence based techniques are more valuable due to their selectivity, sensitivity, cost efficiency and real-time detection.[5] Over the years, a number of fluorescent materials have been reported based on small organic molecules, conjugated polymers and metal-organic frameworks that show selective turn-off response towards PA.[6] However, turn-off sensing method is generally less desired as it offers a lower sensitivity and/or selectivity in presence of other competing nitro-analytes. Thus, it is necessary to develop selective and sensitive turn-on sensors for nitro-explosives, although a few sensors based on turn on responses have been reported for PA recently.[7] Keeping this in mind, we have designed a new molecule on a phosphoramide tripodal backbone, [(NHAQ)$_3$P=O] (TAQP), having an electron-rich aminoquinoline (AQ) chromophore. This compound at lower concentration (1x10^{-5}M) shows a selective ratiometric turn-on response towards PA whereas at higher concentration (1x10^{-3}M) shows a turn-off response for its excimer peak. Interestingly, the turn-on response for PA has been observed for the aqueous systems at 1x10^{-5}M concentration. To the best of our knowledge, this is the first report for a concentration dependant turn-on and off type detection of PA in both protic and non-protic media.

Result and Discussion

Crystal Structure

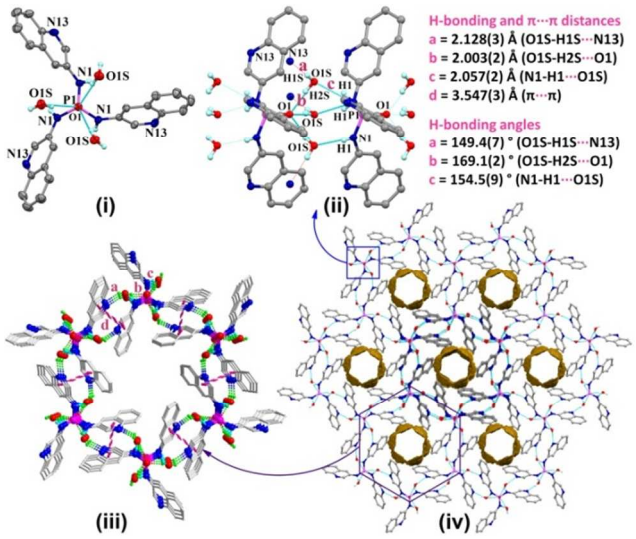

Fig. 1 (i) Crystal structure of TAPQ·3H$_2$O at 50% ellipsoid probability; (ii) formation of 1D-chain structure mediated by O-H…O interactions; (iii) and (iv) view of the hexagonal packing structure mediated by O-H..N and π…π interactions.

The title Compound tris(3-aminoquinolino)phosphorictriamide (TAQP) was synthesized by the reaction of PCl_5 with 3-aminoquinoline in toluene followed by hydrolysis and was characterized by ^{31}P-NMR, mass-spectrometry and single-crystal X-ray diffraction (SC-XRD) (Scheme S1 and Figures S1-S2, ESI). The SC-XRD analysis revealed that the compound was crystallized as TAQP·3H_2O in the trigonal space group P-3 (Tables S1-S3, ESI). The ligand core exhibits a C_3 symmetric backbone along the axis of the P=O bond. The phosphoryl oxygen atom (O1) is involved in a trifurcated H-bonding interaction with all the three solvated water molecules (O1S-H2S) along the three-fold axis and these water molecules connect the adjacent N-H fragments to form a 1D-chain structure (Figures $1_{(i)}$ and $1_{(ii)}$). Interestingly, a hexagonal 3D-lattice (pseudo S6 symmetry) was obtained due to the O-H…N type H-bonding interaction of the remaining proton (H1S) of the water molecules with the N-donor sites (N13). In addition, it shows strong inter-sheet π…π stacking interactions between two adjacent AQ fragments (Fig. $1_{(iii)}$). The packing diagram of it shows a hexagonal open-channel structure, along the c-axis, having a void space of 201.3 Å^3 which amounts to 14.3% of the unit-cell volume (Figure $1_{(iv)}$).

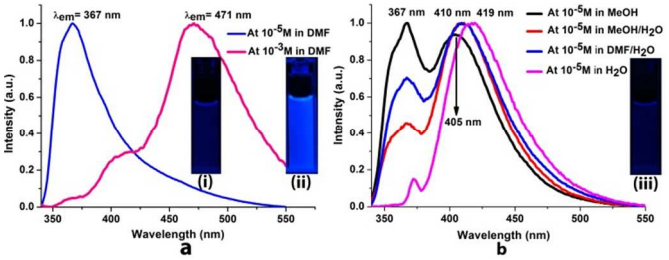

Fig. 2 Emission spectra of various samples of TAQP (λ_{ex} = 330 nm); insets show the emission colours under UV-lamp (λ_{ex} = 365 nm) in (i) 1x10^{-5}M solution of DMF, (ii) 1x10^{-3}M solution of DMF and (iii) 1x10^{-5}M solution of DMF/H_2O or MeOH/H_2O.

Photo-physical Studies

The UV-Visible spectrum of 1x10^{-5}M solution of TAQP in both DMF and MeOH shows an absorption maximum at 330 nm characteristics of the AQ chromophore (Fig. S3-S4 ESI). However, the fluorescence spectrum in MeOH shows two emission peaks at 367 and 405 nm (λ_{ex} = 330 nm), while only one peak at 367 nm was observed in DMF. This indicates the possibility of an H-bonded aggregation for TAQP in a protic solvent such as MeOH even at concentrations as low as 1x10^{-5}M. Further, the emission spectra of TAQP recorded in DMF/H_2O (6:4) and MeOH/H_2O (6:4) mixtures revealed the same trend as two distinct emission peaks were obtained in both instances: 367 and 408 nm in DMF/H_2O and 367 and 410 nm in MeOH/H_2O.[8] Noticeably, the peak around 405 nm was more prominent as compared to parent peak at 367 suggestive of a stronger H-bonding in presence of water. In fact, in neat H_2O suspensions the peak due to aggregation (at 419 nm) was alone prominent and the 367 nm emission got almost diminished. To further check this aggregation phenomenon, the emission spectra was recorded at higher concentrations, 1x10^{-4}M and 1x10^{-3}M, of TAQP. Interestingly, at 1x10^{-3}M concentration of TAQP a large Stoke's shifted (100 nm) peak at 470 nm was observed in both DMF and MeOH in addition to weak emission signals at 367 and 405 nm. This new red shifted peak is attributed to the formation of excimer complex at 1x10^{-3}M which is absent at both 1x10^{-4}M and 1x10^{-5}M concentrations of TAQP (Fig. 2 and S5-S8, ESI).[9] Formation of this excimer emission can be attributed to a strong aggregation of the TAQP molecules at this concentration, mediated by the rich H-bonding and π…π interactions as observed from its crystal structure (Figure $1_{(iv)}$).

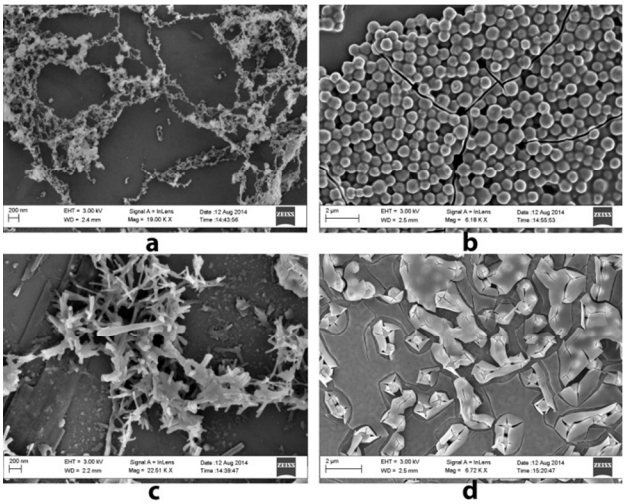

Fig. 3 FESEM images of 1x10^{-5}M solution of TAQP in MeOH (a) before and (c) after the addition of PA; FESEM images of 1x10^{-3}M solution of TAQP in DMF (b) before and (d) after the addition of PA.

To further confirm this aggregation phenomenon, the field emission scanning electron microscopy (FESEM) images were recorded for the TAQP films prepared from both non-aqueous and aqueous media in each of these concentrations. The FESEM images of the TAQP samples prepared from 1x10^{-5}M solutions indicate that the aggregation is dominant in aqueous systems (MeOH/H_2O (6:4) or DMF/H_2O (6:4) compared to those prepared from neat DMF. However at higher (1x10^{-3}M) concentration, strong aggregation can be seen in both protic and aprotic media forming uniform spherical particles of about 800 nm in size. These observations strongly suggest that the non-covalent interactions such as H-bonding and π…π interactions are prevalent at higher solution concentrations of TAQP (Figure 3, Fig. S9 and ESI). The fluorescence decay measurements in neat DMF reveal that the lifetime of the excimer peak at 467 nm in the higher concentration is longer (τ_1=4.25 and τ_2=12.31 ns) compared to that of the 367 nm peak (τ_1=1.09 and τ_2=4.47 ns) in the lower concentration (Fig. S10, ESI).

Picric acid sensing

Prompted by the rich photophysical behaviour of TAQP and the presence of multiple basic N-donor sites in it, we were interested in exploring its potential as PA sensor in both 1x10^{-}

^{5}M and 1x10^{-3}M solution concentrations. Upon the titration of the 1x10^{-5}M solution of TAQP in DMF, the 367 nm emission gradually decreased and a new peak at 465 nm was observed after the addition of 2.5 equivalents of PA. At 5 equivalents of PA concentration, the peak at 367 nm is almost diminished as the new peak at 465 nm becomes dominant signifying a ratiometric fluorescence response. Similar behaviour was observed when the titration was performed in MeOH showing the peaks at 367 and 405 nm were quenched with the onset of the new peak 465 nm (Fig. 4 and S11-S12, ESI).

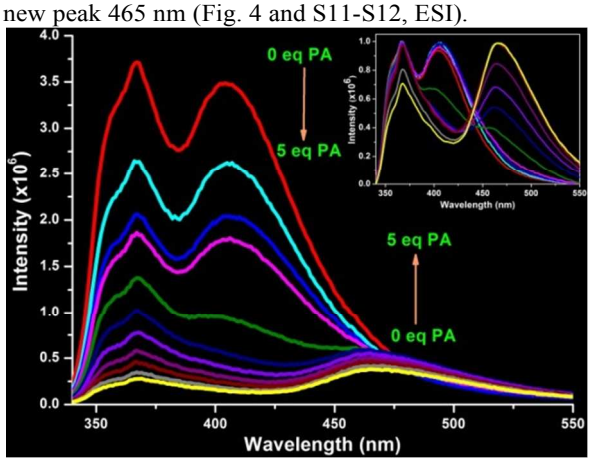

Fig. 4 Emission spectrum of TAQP in MeOH with addition of 5 equivalents PA; inset: normalised spectrum showing the new emission peak at 465 nm.

Time decay measurements at this new peak gave a higher life time values of τ_1=3.88 and τ_2=10.62 ns, indicating a stronger interaction between TAQP and PA (Fig. S10, ESI). Concurrently, the 330 nm peak in the UV-visible spectrum of TAQP (in DMF or in MeOH) was found to be gradually red-shifted to an intense 360 nm peak with the incremental addition of PA (Fig. S13-S14, ESI). These observations point to the fact that the origin of the new peak at 465 nm can be attributed to the protonation of the N-donor sites at TAQP by PA.

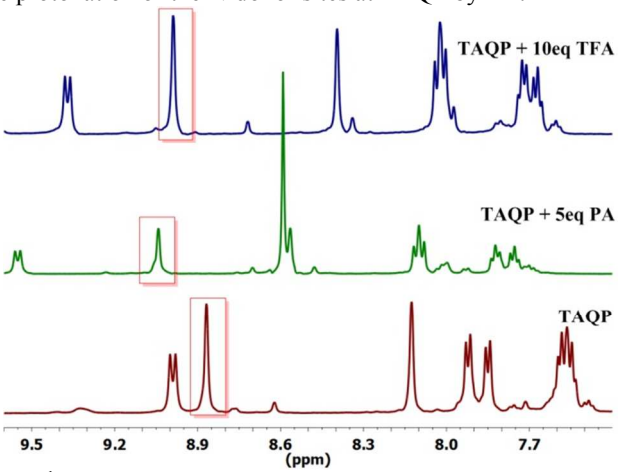

Fig. 5 ^{1}H-NMR of TAQP (brown) in presence of PA (green) and TFA (blue) in DMSO-d_6. The signals marked in boxes are the aromatic protons adjacent to the N-donor sites.

To validate this, the emission spectral titrations of TAQP were performed in presence of trifluoroacetic acid (TFA), a comparably strong acid as that of PA.[7b] These again showed a ratiometric turn-on response, similar to that of PA, upon the addition of 5 equivalents of TFA. Further, the ^{1}H-NMR spectra of TAQP in presence of 10 equivalents TFA showed a downfield shift for the AQ protons. A similar downfield shift was observed for the TAQP sample containing 5 equivalent of PA as well. Thus, both these results strongly suggest that TAQP exhibits a ratiometric fluorescence response due to proton transfer from acidic PA to the N-donor sites of the AQ moieties (Fig. 5 and S15-S17, ESI). Also it is interesting to note that TFA shows only ratiometric fluorescence response whereas PA largely quenched the emission due to the AQ chromophore. This is due π…π interaction between PA and quinoline moiety which results in an effective energy transfer from AQ to PA. This interaction was clearly visible in FESEM image in which a better and different kind of aggregation was observed for TAQP (1x10^{-5}M) treated with 5 equivalents of PA (Fig. 3). Also, titration experiments were performed in aqueous systems containing DMF/H_2O (6:4) or MeOH/H_2O (6:4) which again gave the ratiometric response with the formation of peak at 465 nm (Fig. S18-S20, ESI.). Further, titration experiment with PA in neat H_2O suspensions (1x10^{-5}M) showed a facile ratiometric response wherein the 419 nm aggregation peak was completely shifted to a new peak due to protonation at 464 nm (Fig. 6 and S21, ESI). The detection limit for this aqueous phase sensing in neat H_2O and DMF/H_2O mixture was found to be 0.2 and 0.13 ppm, respectively (Fig. S22, ESI).[7a]

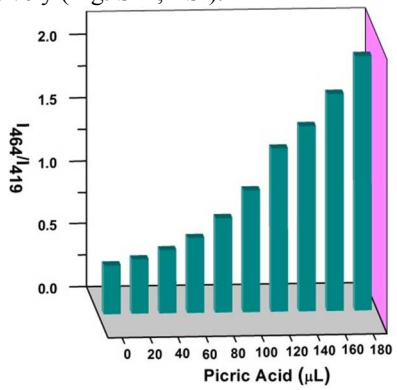

Fig. 6 Relative changes of fluorescent intensity (I_{464}/I_{419}) of TAQP (1x10^{-5}M) for PA in neat H_2O suspension.

Similar PA titrations with the 1x10^{-3}M of TAQP solution shows only a quenching behaviour. Thus, a gradual decrease in excimer 465 nm peak was observed for the incremental addition of PA with no apparent shift in its emission maxima. This observation suggests that the acidic protons of PA could not disrupt the strong inter-molecular H-bonding present in the higher concentrations of TAQP and thus could not protonate the N-donor sites present in it. However, PA can interact with the surface aromatic groups of the AQ moieties via π…π interactions and can quench its luminescence emission.[6e] This is in fact evident from the FESEM image of the TAQP (1x10^{-3}M) treated with PA (20 eq.) which showed that the hollow spherical aggregation was retained as these particles were merely covered with the PA layers (Fig. 3, S23-S24, ESI). To

check the selectivity of TAQP towards PA, titration experiments have been performed for other nitro-analytes such as nitrobenzene (NB), dinitrobenzene (DNB), nitrotoluene (NT), dinitrotoluene (DNT), trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX) and nitrophenol (NP). These titrations show negligible luminescence quenching for most of the analytes except for NP. For NP only a moderate quenching behaviour and no ratiometric/turn-on response was observed for a 1x10^{-5}M TAQP solution (Fig. S25-S33, ESI).

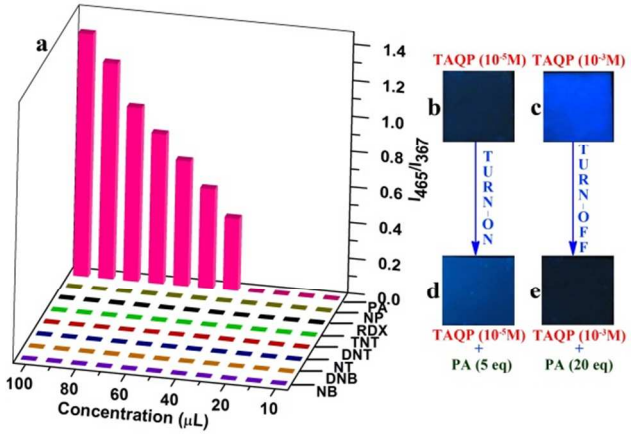

Fig. 7 (a) Relative changes of fluorescent intensity (I_{465}/I_{367}) of TAQP (1x10^{-5}M) for PA and other possible interfering analytes; (b)-(e) emission colours under UV-lamp for TLC plates treated with TAQP and TAQP+PA at different concentrations.

Furthermore, the selectivity of TAQP towards PA in the presence of other interfering analytes has been determined from luminescence titration with mixed nitro-analytes (Fig. 8). It is evident from these titrations that only PA can show the ratiometric response while the other analytes exhibit negligible changes in emission. Further, the obtained Stern-Volmer constant (K_{sv}) value of 2.8x10^5 M^{-1} for this ratiometric sensing is quite high and is comparable with other recently reported PA sensors.[10] The sensing selectivity of TAQP for PA in presence of other interfering aromatics functionalities such as 4-bromobenzoic acid (4-BBA), 4-nitrobenzoc acid (4-NBA), benzaldehyde (Bz), 4-nitrobenzaldehyde (4-NBz) and 4-Naphthol (4-NpOH) have also been tested which again showed the ratiometric response for only PA (Fig. S34, ESI).

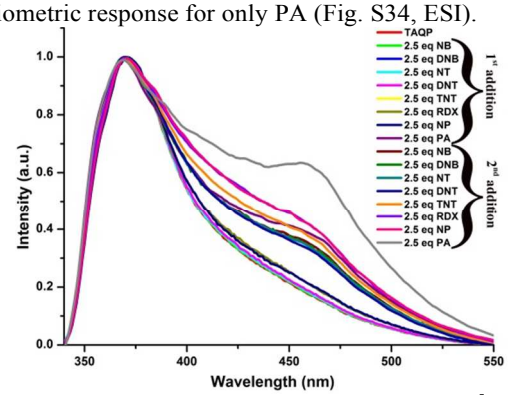

Fig. 8 Emission spectral titration of TAQP (1x10^{-5}M) of PA (1x10^{-3}M) in the presence of other interfering nitro-analytes (1x10^{-3}M) in DMF.

Conclusion

In summary, we present a simple aminoquinoline containing tripodal phosphoramide ligand which shows concentration dependant aggregation due to H-bonding and π…π stacking in both protic and non-protic media. At 1x10^{-5}M concentration, a ratiometric turn-on response was observed for PA with the formation of a new peak at 465 nm due to protonation of its N-donor sites. Further, TAQP shows a high selectivity in ppm levels towards PA in aqueous media as well as in presence of other interfering nitro-explosives and has the potential to act as a PA probe for real-time application.

Experimental Section

General Remarks

All manipulations involving phosphorus halides were performed under dry atmosphere in standard Schlenk-glassware. 3-aminoquinoline was purchased from Aldrich and used as received. PCl_5 and $POCl_3$ was purchased locally (SPECTROCHEM, India) and used as received. NMR spectra were recorded on a 400 MHz Jeol FT spectrometer (^{1}H-NMR: 400.13 MHz, ^{13}C{^{1}H}-NMR: 100.62 MHz, ^{31}P{^{1}H}-NMR: 161.97 MHz) at room temperature using $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. Thermal analysis data has been obtained from a Perkin-Elmer STA-6000 thermogravimetric analyser. Elemental analyses were performed on a Vario-EL cube elemental analyser. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer. The absorption and emission studies were done by a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer and SPEX Flurolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m SPEX 1680 monochromator and a 450W Xe lamp as the excitation source. The excitation and emission spectra of the complexes were corrected at instrumental function. The photoluminescence lifetime measurements were carried out using a SPEX Flurolog HORIBA JOBIN VYON 1934 D phosphorimeter. The luminescent lifetime of TAQP was measured by Time Correlated Single Photon Counting (TCSPC) method at 298K. The 298K luminescence decay profiles were fitted to biexponential curves. Similarly, the lifetimes were fitted by using the DAS software.

Synthesis of TAQP

To a stirred solution of 3-aminoquinoline (6.92g, 0.048 mol) in toluene (150 mL), PCl_5 (1g, 0.0048 mol) in toluene (50 mL) was added drop wise for 30 minutes. The resulting mixture was refluxed at 110^0 C for 12 h to yield a yellow precipitate. The precipitate was collected by filtration and washed with excess of water to remove the amine-hydrochloride by-product. The resulting powder was treated with NaOH solution in methanol and washed with water. The obtained yellow powder was dried in vaccum and collected. The crystals suitable for X-ray analysis were obtained from its solution in methanol. Yield: 66% (1.20 g based on P). ^{1}H-NMR (400 MHz, $(CD_3)_2SO$: δ 7.56 (dd, 3H, C*H*), 7.58 (dd, 3H, C*H*), 7.85 (d, 3H, C*H*), 7.92 (d, 3H, C*H*), 8.13 (s, 3H, C*H*), 8.87 (s, 3H, C*H*) 8.99 (d, 3H,

N*H*). ^{31}P NMR (161 MHz, {$(CD_3)_2SO$}): δ -4.02. FT-IR data in KBr pellet (cm^{-1}): 3100, 1605, 1575, 1511, 1457, 1410, 1346, 1207, 1184, 1139, 1105, 993, 940, 891, 865, 620, 569. Anal. calcd. for $C_{27}H_{21}N_6OP$: C, 68.06; H, 4.44; N, 17.64. Found: C, 67.96; H, 4.56; N, 16.61.

Crystallography

Reflections of TAQP.3H_2O were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoKα radiation (λ = 0.71073 Å) (Table S1, supporting information). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).[11] All non-hydrogen atoms were refined aniostropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. Crystals of 1 diffracted weakly at higher angles and hence a 2θ = 50 ° cut-off was applied.

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Notes and references

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Electronic Supplementary Information (ESI) available: experimental details, additional figures and tables. CCDC 1024970. For ESI and crystallographic data in CIF format see DOI: 10.1039/c000000x/

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