Anion Coordination

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Anion-Coordination-Induced Turn-On Fluorescence of an Oligourea-Functionalized Tetraphenylethene in a Wide Concentration Range**

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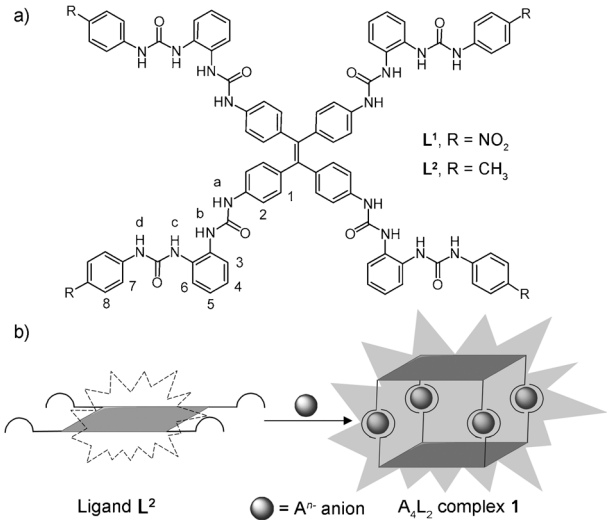
Abstract: *A tetrakis(bisurea)-decorated tetraphenylethene (TPE) ligand (**L²**) was designed, which, upon coordination with phosphate ions, displays fluorescence "turn-on" over a wide concentration range, from dilute to concentrated solutions and to the solid state. The fluorescence enhancement can be attributed to the restriction of the intramolecular rotation of TPE by anion coordination. The crystal structure of the A_4L_2 (A = anion) complex of **L²** with monohydrogen phosphate provides direct evidence for the coordination mode of the anion. This "anion-coordination-induced emission" (ACIE) is another approach for fluorescence turn-on in addition to aggregation-induced emission (AIE).*

The search for efficient luminescent materials continues to be a topic of great interest.[1] Many fluorescent chromophores show strong emission in dilute solutions but are only weakly or non-emissive in concentrated solutions or the solid state owing to aggregation-caused quenching (ACQ).[2] In 2001, Tang and co-workers discovered "aggregation-induced emission" (AIE) for some compounds which are non-luminescent in solution but are emissive in the aggregated state.[3] Since this pioneering work, AIE luminogen molecules have attracted much attention in fluorescent sensors, biological probes, and solid-state lighting materials.[4] The AIE phenomenon is primarily caused by the restriction of intramolecular rotation (RIR) which activates the fluorescence. This implies that the fluorescence might also be switched on by restrictions other than aggregation, such as the recently reported metal coordination or metal-anion binding.[5]

Anion coordination chemistry has developed rapidly because of the relevance of anions in many areas, such as in biology, medicine, and the environment.[6] Phosphates (lipid phosphates, inorganic phosphates, and phosphate esters) are ubiquitous in biological systems and play important roles in membrane integrity, bone mineralization, cellular signaling, muscle function, and other vital biological processes.[7] Inorganic phosphates (P_i) are crucial for the maintenance of phosphate balance and homeostasis of the body and are involved in most metabolic processes and enzymatic reactions.[8] Therefore, the study of phosphate-ion coordination is very important for understanding cellular activities.

We have recently reported a class of *ortho*-phenylene-bridged[9] oligourea ligands, which display excellent coordination properties with phosphate in terms of coordination geometry and coordination number.[10] The similarities to transition-metal coordination[6b] suggest that anion complexes might also find applications in various fields. To explore the potential of these oligourea ligands in fluorescent materials and biosensors (e.g. for the detection of phosphate), we designed tetrakis(bisurea) derivatives **L¹** and **L²**, in which four bisurea moieties are attached to a tetraphenylethene (TPE) core (Scheme 1). It is expected that the rotation of the phenyl rings of TPE about the ethene core would be restricted by anion coordination, thereby turning on the fluorescence. TPE is a well-studied, iconic AIE chromophore.[11] However, the deliberate design of fluorescent anion complexes with the TPE backbone have not yet been reported. Herein, we present the fluorescence turn-on properties of ligand **L²** in a wide concentration range through coordination to phosphate ions, which can be regarded as "anion-coordination-induced emission" (ACIE).



Scheme 1. a) Structural formula of ligands **L¹** and **L²**; b) Schematic illustration of the anion-coordination-induced emission.

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Initially, the nitrophenyl-substituted ligand $\mathbf{L^1}$ (Scheme 1) was chosen as this substituent can enhance the anion binding ability of the urea groups.[10] However, $\mathbf{L^1}$ showed very weak emission even at high concentrations (Figure S20 in the Supporting Information), possibly owing to the electron-withdrawing effect of the nitro group. Therefore, the nitro groups were replaced by methyl and $\mathbf{L^2}$ was synthesized (Scheme 1; see Supporting Information for synthetic details). Ligand $\mathbf{L^2}$ displayed almost no emission in dilute solution, but the intensity of fluorescence at $\lambda = 500$ nm ($\lambda_{ex} = 429$ nm) was significantly enhanced by increasing the concentration or adding a poor solvent (Figure S20, S21), which is typical of AIE activity.

Interestingly, ligand $\mathbf{L^2}$, non-emissive in the absence of anions in dilute solution (1×10^{-5} M, DMSO), started to exhibit fluorescent emission upon gradual addition of phosphate ions. When 10 equivalents of PO_4^{3-} or 16 equivalents of HPO_4^{2-} ions (generated in situ from (TBA)OH and $(TBA)H_2PO_4$, TBA = tetrabutylammonium) were added, the fluorescence intensity showed maximum enhancement, by approximately 27- and 20-fold, respectively (Figure 1). The

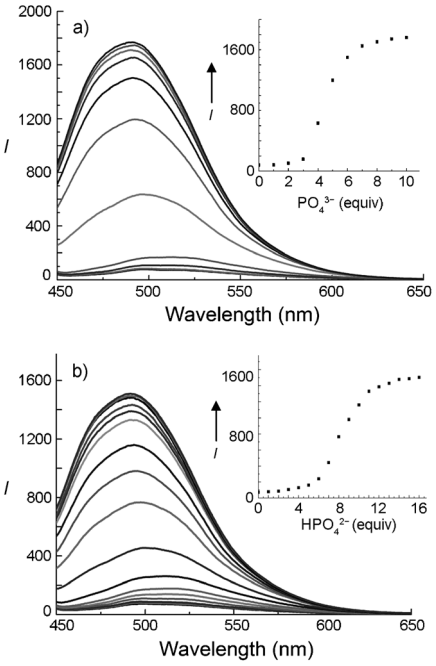

Figure 1. Fluorescence emission spectra ($\lambda_{ex} = 429$ nm) of $\mathbf{L^2}$ (10 μM in DMSO) upon addition of a) 0–10 equiv of PO_4^{3-}; and b) 0–16 equiv of HPO_4^{2-}. Insets: The increase of fluorescence intensity at $\lambda = 494$ nm.

binding of $\mathbf{L^2}$ with various other anions was also examined. The addition of 10 equivalents of SO_4^{2-} ions resulted in an approximately 50% enhancement of the fluorescence intensity (by 13-fold), while other anions induced either no obvious change (NO_3^-, Br^-, Cl^-, ClO_4^-, I^-, and HSO_4^-) or only slight enhancement (CO_3^{2-}, as $[K([18]crown\text{-}6)]^+$ salt; HCO_3^-, as $[Na([15]crown\text{-}5)]^+$ salt; $H_2PO_4^-$, AcO^-, and F^-, as TBA^+ salts; 10 equiv; Figure 2).

Moreover, competition experiments were conducted for the system composed of $\mathbf{L^2}$ and 10 equivalents of phosphate

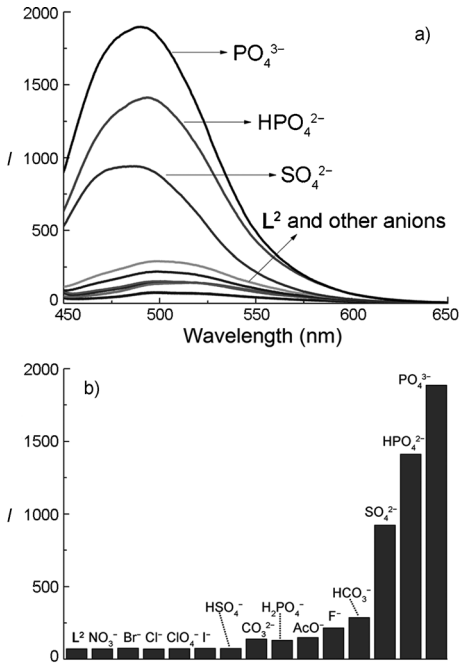

Figure 2. a) Fluorescence emission spectra ($\lambda_{ex} = 429$ nm) of $\mathbf{L^2}$ (10 μM in DMSO) upon addition of various anions (10 equiv); b) Variation of fluorescence intensity at $\lambda = 494$ nm.

ions (PO_4^{3-} or HPO_4^{2-}) by adding 100 equivalents of other anions. The emission intensity was not affected by a 10-fold excess of NO_3^-, Br^-, Cl^-, ClO_4^-, and I^- but was partially quenched by HSO_4^-, CO_3^{2-}, AcO^-, HCO_3^-, and F^-. However, the fluorescence was almost turned off when 100 equivalents of SO_4^{2-} ions were present (Figure S22).

In addition, ^1H NMR spectroscopic studies were carried out to study the interactions of these anions with $\mathbf{L^2}$. Addition of SO_4^{2-} and CO_3^{2-} ions (10 equiv) to $\mathbf{L^2}$ caused large downfield shifts of the resonance signals arising from the urea NH protons, comparable to the shifts induced by HPO_4^{2-}, while AcO^-, HCO_3^-, or $H_2PO_4^-$ ions resulted in moderate downfield shifts. The ^1H NMR spectrum of $\mathbf{L^2}$ showed no change or slight changes in the presence of 10 equivalents of NO_3^-, Br^-, ClO_4^-, I^-, HSO_4^-, Cl^-, or HCO_3^- ions, implying very weak binding. Deprotonation of the urea NH groups was observed upon addition of 10 equivalents of F^- ions to $\mathbf{L^2}$ (Figure S15, S16).

The results of both NMR and fluorescence studies indicate that the presence of other anions has different influences on the fluorescence of the $\mathbf{L^2}$–phosphate system. The Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- ions exhibited weak binding by $\mathbf{L^2}$ and thus did not affect the fluorescence. The SO_4^{2-} and CO_3^{2-} ions alone showed rather strong binding to $\mathbf{L^2}$ but less fluorescence enhancement, suggesting that the coordination mode may be different from (less restricting than) that of the phosphate ion in solution. Nonetheless, these anions can affect the fluorescence of the phosphate system through competitive binding to the ligand. The situation for the other anions, such as HSO_4^-, F^- and HCO_3^-, may be more complicated because of the possibility of multiple protona-

tion/deprotonation processes, which also interfere with the phosphate coordination and the fluorescence properties.

To further understand the coordination mode of $\mathbf{L^2}$ with phosphate and how it restricts the intramolecular rotation, single crystals were grown of the monohydrogen phosphate complex $[K([18]crown\text{-}6)]_8[(HPO_4)_4(\mathbf{L^2})_2]$ (**1**) from $\mathbf{L^2}$, K_3PO_4, and [18]crown-6.[12] The existence of phosphate in its monoprotonated form is confirmed by the eight $[K([18]crown\text{-}6)]^+$ countercations and by the hydrogen-bond-donor character of one of the oxygen atoms (see below). Efforts to crystallize the orthophosphate complex have so far been unsuccessful even under more basic conditions.

Complex **1** shows a 4:2 anion-to-ligand ratio, in which the four HPO_4^{2-} ions are sandwiched by two ligand molecules stacking in a face-to-face fashion (Figure 3a,b). In the C_2-symmetric complex (space group $C222_1$), the four terminal bisurea arms of each ligand point to the same side of the rectangular TPE moiety, entangling with the bisurea groups of the other ligand to coordinate the anions. The P···P separations between phosphate groups are 8.18 and 14.00 Å, and the distance between the central vinyl groups of the two ligands is 5.78 Å. The TPE cores of the two ligands are in a slightly staggered conformation, with a torsion angle of 18.0° between the two C=C bonds. The four HPO_4^{2-} ions display two different coordination environments. Two (C_2-related) HPO_4^{2-} ions (P2 and P2B) are each coordinated by two bisurea moieties through a total of twelve N–H···O hydrogen bonds, seven of which have N···O distances less than 3.2 Å and the other five in the range 3.2–3.5 Å. The other type of HPO_4^{2-} (P1 and P1A) is also coordinated by four urea groups (through eight N–H···O hydrogen bonds with N···O distances in the range 2.7–3.2 Å). There is an additional contact from one O atom of the anion to a K^+ countercation.

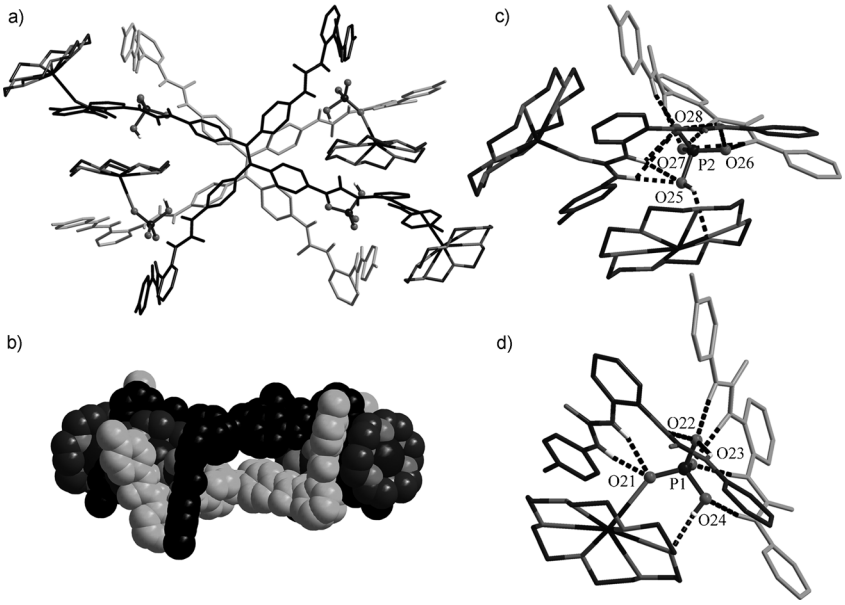

Figure 3. Crystal structure of $[(HPO_4)_4(\mathbf{L^2})_2]^{8-}$ (**1**). a) The coordination of four HPO_4^{2-} ions by two ligands; b) Side view of the space-filling representation; c,d) Hydrogen bonds (broken lines) around the HPO_4^{2-} ions.

Notably, the HPO_4^{2-} ions are not only hydrogen-bond acceptors but also hydrogen-bond donors, forming a P–OH···O bond with one crown ether oxygen atom (O···O bond length 2.885(9) and 2.771(7) Å, O–H···O angle 101.3° and 166.8°; Figure 3c,d). This binding mode is quite similar to the phosphate-binding protein (PBP), which forms twelve hydrogen bonds with a HPO_4^{2-} ion including one from the OH of the anion.[13] Moreover, two CH···π interactions are formed between the terminal *p*-tolyl rings and the bridging *o*-phenylene planes within the A_4L_2 unit, with CH···plane distances of 3.84–3.98 Å (Figure S9), in a similar range to those observed in our previous work.[10]

The crystal structure clearly shows that the TPE chromophore is "fixed" by the HPO_4^{2-} coordination to the bisurea arms, while the fluorescence of complex **1** increased greatly compared to ligand $\mathbf{L^2}$ (Figure 4). However, for an unambiguous assignment of whether the fluorescence turn-on is caused by anion coordination or by aggregation, more evidence is necessary. An inspection of the solid-state packing structure of complex **1** indicates that the shortest phenyl···phenyl separation between the two TPE cores within one A_4L_2 complex is 3.778 Å (C17···C64; Figure S11). This "intramolecular" (from the viewpoint of the anion complex **1**) contact may be a result of the anion coordination that brings the two ligands together. The distance is slightly longer than the closest phenyl···phenyl contact (3.4 Å) observed for TPE derivatives, while larger separations (4.7 Å) were reported for MOFs (metal–organic frameworks) with TPE cores, in which the fluorescence enhancement is attributed to metal coordination.[5a] However, the shortest contact between the phenyl rings of TPE in two adjacent A_4L_2 moieties is much longer, at 9.89 Å (Figure S10), suggesting that there is essentially no further "intermolecular" contact of the TPE chromophores even in the solid-state structure. Therefore, the fluorescence can be attributed to the restriction effect of the sandwiched anion

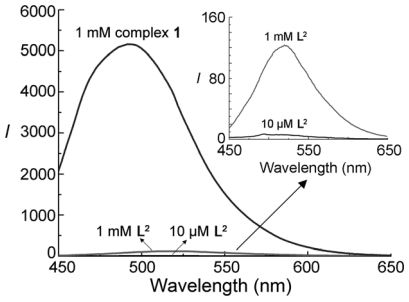

Figure 4. Fluorescence emission spectra of $\mathbf{L^2}$ (10 μM and 1 mM in DMSO) and complex **1** (1 mM in DMSO). Inset: magnified curves (fluorescence intensity = 0–160).

coordination. In other words, the solid-state anion complex **1**, the dimer, can be viewed as the smallest aggregate of TPE, and gives rise to strong emission, fivefold higher than that of $\mathbf{L^2}$ (Figure S23).

In addition, dynamic light scattering (DLS) measurements revealed no significant change in the light-scattering intensity when 10 equivalents of PO_4^{3-} or HPO_4^{2-} ions were added to $\mathbf{L^2}$, despite the obvious enhancement of the fluorescence (Figure S24). On the other hand, when water (a poor solvent for $\mathbf{L^2}$) was introduced to the solution of $\mathbf{L^2}$, the fluorescence intensity (in DMSO-90% H_2O) increased by only a factor of five compared to that in DMSO (1×10^{-5} M; Figure S21). However, the DLS intensity displayed a large increase (about 14 times that caused by PO_4^{3-} or HPO_4^{2-} ions), implying that the aggregation of $\mathbf{L^2}$ itself in the free ligand has little contribution to the fluorescence. These results further confirm that the large fluorescence enhancement is predominantly induced by anion coordination rather than the aggregation of $\mathbf{L^2}$.[5b]

The ^{1}H NMR spectrum of complex **1** in [D$_6$]DMSO displays large downfield shifts ($\Delta\delta = 1.88$–2.80 ppm; Figure S13) for all of the resonance signals arising from urea NH protons compared to the free ligand $\mathbf{L^2}$. The ^{1}H NMR titration experiment (Figure S14) showed a slow exchange process with broadened NH signals for the formed anion complex. The signals became well-resolved when 2.0 equivalents of HPO_4^{2-} ions were added, and no further change was observed with more HPO_4^{2-}. The spectrum is very similar to that of complex **1**, indicating the formation of the 1:2 (host/guest) species. Moreover, the NOESY spectrum of complex **1** (Figure S17, S18) reveals cross-peaks between H6-H7/H8, H4/H5–H7, and H4/H5–H8 (see Scheme 1 for the proton numbering) on the terminal *p*-tolyl and bridging *o*-phenylene rings, respectively, because of through-space coupling interactions. These interactions suggest that the A_4L_2 complex may be persistent in solution. This is further supported by the Job's plot of the fluorescence spectra at $\lambda = 505$ nm, which gives a 1:2 (2:4) stoichiometry (Figure S25), consistent with complex **1**.

The change in the emission intensity of complex **1** with varying concentration (from 10 μM to 1 mM in DMSO) displays very interesting features. In dilute solutions (10 μM to 0.1 mM), the fluorescence intensity showed a nearly linear increase. After 0.25 mM, the fluorescence increased slightly and reached a plateau at about 1 mM (Figure S27). Therefore, the fluorescence of ligand $\mathbf{L^2}$ can be "turned on" by phosphate in a rather wide concentration range, from dilute to concentrated solutions as well as in the solid state, which is significantly different from both the ACQ and AIE chromophores. The quantum yields (Φ) of $\mathbf{L^2}$ and complex **1** in solution (1×10^{-4} M, DMSO) are 9.1% and 41.3%, respectively, as measured using an integrating sphere (Table S4).

Efforts have also been made to synthesize complexes of other anions, and a similar A_4L_2 (A = anion) complex of carbonate, $[K([18]crown\text{-}6)]_8[(CO_3)_4(\mathbf{L^2})_2]$ (**2**), has been isolated. Complex **2** (space group *C*2/*c*) is essentially isostructural to the HPO_4^{2-} analogue **1** (Figure S12). There are also two types of coordination mode for the four CO_3^{2-} ions: with or without the anion–K coordination to the $[K([18]crown\text{-}6)]^+$ cations. Two C_2-related CO_3^{2-} anions are each coordinated by four urea groups through nine N–H···O hydrogen bonds, as well as by an O–H···O bond (O···O distance 2.744(7) Å) to a water molecule that is coordinated to a K^+ countercation. The other two CO_3^{2-} anions are each coordinated by four urea groups through ten N–H···O hydrogen bonds. Solution binding studies demonstrated that ten equivalents of CO_3^{2-} ions induced only a slight fluorescence enhancement and the maximum intensity was observed with 120 equivalents of CO_3^{2-} ions (11-fold increase; Figure S26), possibly owing to a different binding mode in solution.

In conclusion, we have designed a tetrakis(bisurea) ligand ($\mathbf{L^2}$) that incorporates the tetraphenylethene (TPE) chromophore. The non-emissive ligand $\mathbf{L^2}$ displays a large fluorescence enhancement in the presence of phosphate ions in a wide range of concentrations (dilute and concentrated solutions, and solid state), which is attributable to the restriction of the intramolecular rotation of TPE by anion coordination. This unique "anion-coordination-induced emission" (ACIE) may find application in various areas such as fluorescent sensors. Investigations on other ACIE systems and their applications are currently underway.

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Keywords: anion coordination · fluorescence turn-on · oligourea · phosphate · tetraphenylethene

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[12] Crystal data for complex **1**: red-brown block, $C_{280}H_{388}K_8N_{32}O_{88}P_4$, $M = 6046.90$, orthorhombic, space group $C222(1)$, $a = 29.419(6)$, $b = 44.908(9)$, $c = 28.031(5)$ Å, $V = 37033(12)$ Å^3, $T = 150$ K, $Z = 4$, 114503 refl. collected, 31522 unique ($R_{int} = 0.0799$), $R1 = 0.1172$ ($I > 2\sigma(I)$), $wR2 = 0.3215$ (all data). Crystal data for complex **2**: yellowish-brown block, $C_{138}H_{177}K_4N_{17}O_{39}$, $M = 2854.37$, monoclinic, space group $C2/c$, $a = 44.964(12)$, $b = 27.634(7)$, $c = 27.188(7)$ Å, $\beta = 91.159(8)°$, $V = 33776(15)$ Å^3, $T = 150$ K, $Z = 8$, 135746 refl. collected, 28561 unique ($R_{int} = 0.0948$), $R1 = 0.1249$ ($I > 2\sigma(I)$), $wR2 = 0.2987$ (all data). CCDC 985431 (**1**) and 985432 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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