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Synthesis and luminescence properties of a series of tris(4-styrylphenyl)phosphorus-(III) and -(V) compounds and of a $[Cu(PR_3)_4]BF_4$ complex †

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The series of compounds PR_3, $O{=}PR_3$, MeR_3PI, Cl_2PR_3 and $[Cu(PR_3)_4]BF_4$ (R = (*E*)-4-(4-*tert*-butylstyryl)phenyl) has been prepared and optical properties explored by absorption and fluorescence spectroscopy. The effect of geometry and coordination number on luminescence intensity is presented.

Introduction

Materials incorporating extended π-conjugation have attracted a great deal of attention recently. Such materials display a diverse set of electronic properties, spanning the range from insulating to conducting, while maintaining the facile processability typical of other organic polymers.[1] This unique property set has led to their use in applications ranging from OLEDs and use in display devices,[2] to molecular sensors,[3] wires, and switches for molecular electronics.[1,4] Such extended π conjugation is also a common feature of non-linear optical (NLO) materials, and ligands with π conjugated units tethered to their framework have recently found application in quadrupolar NLO-active metal complexes (two examples, Chart 1).[5]

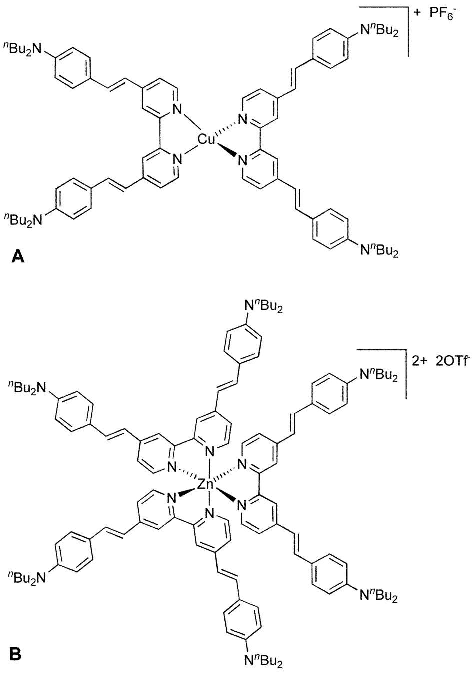

Chart 1

Our ongoing interest in incorporating phosphorus centers into materials with novel opto-electronic properties[6] led us to explore the possibility of creating triphenylphosphine-based ligands having an extended π conjugated system. Such materials could be utilized as fundamental building blocks in extended systems (oligomers, polymers or dendrimers) or as ligands for novel metal complexes with possible NLO activity. Oligomeric or polymeric materials based on such a morphology may be thought of as hybrids between poly(diphenylphosphine) (a phosphorus analogue of polyaniline that has been reported recently)[7] and short sections of poly(phenylenevinylene) (PPV). Both PPV and polyaniline are technologically important π conjugated and conducting polymers, and research aimed at varying the functionality in these materials is an area of extensive current interest.[8]

Previous reports describe amines and phosphines with NLO and/or LED applications.[9] These reports serve as a starting point for designing the system employed in the current study, since they feature the general structural features of interest. Recently, a systematic investigation of absorption and luminescence properties with respect to coordination number and geometry has been carried out on trianthrylphosphorus compounds.[10] At the start of our investigation, we were surprised to find that no tris(styrylphenyl)phosphines were known. While this manuscript was in preparation a report appeared describing synthesis of and study of energy transfer in a tris(4-(4-styrylstyryl))phenyl)phosphine.[11] This study was limited to the triarylphosphine, and not extended to other organophosphorus compounds where one could induce other possible geometries and coordination numbers, however. Furthermore, to our knowledge, none of the previously reported related systems have been used as ligands for metal complexes. We herein present the systematic investigation of the absorption and luminescence behavior exhibited by a series of tris(4-styrylphenyl)phosphorus compounds in a variety of geometries and by a representative metal complex. The availability of various geometries and oxidation states/coordination numbers at the phosphorus center allows some flexibility in the proximity and orientation of bound chromophores (and their associated dipoles) to one another, and may thus allow for switching or tuning of optical properties in these materials.

Experimental

General considerations

All syntheses were carried out either in a glove box or using modified Schlenk line techniques, under an atmosphere of dry N_2. Diethyl ether, THF, hexanes, benzene, and toluene were distilled from benzophenone–Na ketyl under N_2 before use. Acetonitrile was refluxed under N_2 over CaH_2 for 6 h and distilled. Absolute ethanol was dried by stirring over freshly activated powdered 3Å molecular sieves prior to use. Phosphorus trichloride was purified by vacuum transfer. Anhydrous CH_2Cl_2 and *p*-bromobenzaldehyde (Acros) were used as received. Fluorescence measurements were carried out on a SPEX Fluorolog FL3–12 in degassed HPLC grade $CHCl_3$ on solutions with absorbance of approximately 0.10 with an excitation wavelength of 310 nm. Absorption spectra were carried

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† Electronic supplementary information (ESI) available: ^1H, ^{13}C and ^{31}P NMR spectra. See http://www.rsc.org/suppdata/dt/b3/b309735h/

out in the same solvent on a Lambda 25 spectrophotometer. NMR spectra were recorded on a Varian Gemini instrument operating at 300 MHz (^{1}H), 75.5 MHz (^{13}C) and 121.5 MHz (^{31}P). Proton, carbon and phosphorus spectra are referenced to residual solvent signals, $CDCl_3$, and 85% phosphoric acid, respectively.

(*E*)-4-Bromo-4′-*tert*-butylstilbene (TbsBr)

A 0.36 M solution of LiOEt was prepared by placing 0.25 g (36 mmol) of freshly-cut Li metal in 100 mL of anhydrous ethanol and stirring until reaction was complete. To this solution was added a solution of (*p*-*tert*-butylbenzyl)triphenylphosphonium bromide[12] (15.9 g, 32.4 mmol) and *p*-bromobenzaldehyde (6.00 g, 32.4 mmol) in 75 mL ethanol over a 30 min period. The resultant yellow suspension was stirred at room temperature for 6 h, filtered off, and the off-white solid rinsed with cold ethanol and dried to give the product as a mixture of (*E*) and (*Z*) isomers as ascertained by ^{1}H NMR spectroscopy. Transformation to the all-(*E*) form was accomplished by refluxing the material for 3 h in 50 mL toluene in the presence of a crystal of iodine. The solution was then cooled to room temperature, washed with 5% Na_2SO_3. The organic layer was collected and all volatiles removed under reduced pressure to give 7.28 g (71.2%) of the product as an off-white powder: mp 153–155 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9H), 6.99 (d, 1H, J_{HH} = 16 Hz), 7.09 (d, 1H, J_{HH} = 16 Hz), 7.35–7.40 (m, 4H), 7.43–7.48 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.0, 136.4, 134.1, 131.7, 129.2, 127.8, 126.5, 126.3, 125.6, 121.0, 34.6, 31.2. Calc. for $C_{18}H_{19}Br$: C, 68.58; H, 6.07. Found: C, 68.50, H, 6.04%.

PTbs$_3$ (1)

To a solution of (*E*)-4-bromo-4′-*tert*-butylstilbene (5.00 g, 15.9 mmol) in 25 mL THF at −78 °C was added 6.7 mL *n*-BuLi (2.5 *M* in hexanes, 17 mmol) *via* cannula, and the resultant mixture stirred for 1 h. PCl_3 (0.28 mL, 3.2 mmol) was then added to the cold solution via syringe and the mixture was allowed to slowly warm to room temperature. All volatiles were removed *in vacuo* and the resultant orange residue was sequentially rinsed with hexanes, acetonitrile and diethyl ether to afford **1** as a white powder (2.34 g, 77.4%): mp 284–286 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 27H), 7.05 (d, 3H, J_{HH} = 16 Hz), 7.14 (d, 3H, J_{HH} = 16 Hz), 7.30–7.40 (m, 12H), 7.44–7.50 (m, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.0, 138.0, 136.2 (d, J_{PC} = 11 Hz), 134.4, 134.0 (d, J_{PC} = 20 Hz), 129.3, 127.3, 126.5 (d, J_{PC} = 7 Hz), 126.3, 125.6, 34.6, 31.3; ^{31}P{^{1}H} NMR ($CDCl_3$) δ −6.1; HRMS (FAB, *m*/*z*): calc. for $C_{54}H_{57}P$, 737.4276; found, 737.4269. UV-vis: λ_{max} 336 nm (ε = 112 000 M^{-1} cm^{-1}). Calc. for $C_{54}H_{57}P$: C, 88.00; H, 7.80. Found: C, 88.18, H, 7.84%.

O=PTbs$_3$ (2)

A suspension of PTbs$_3$ (100 mg, 0.136 mmol) in 10 mL 15% H_2O_2 in 1 : 1 EtOH–H_2O was stirred overnight. Excess peroxide was quenched by addition of 5% aqueous Na_2SO_3, and the organics extracted in chloroform. Removal of volatiles under reduced pressure affords the product as a fine white powder (89 mg, 87%): mp 290–292 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 27H), 7.08 (d, 3H, J_{HH} = 16 Hz), 7.20 (d, 3H, J_{HH} = 16 Hz), 7.40 (d, 6H, J_{HH} = 8 Hz), 7.47 (d, 6H, J_{HH} = 8 Hz), 7.57–7.70 (m, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.5, 141.1, 133.9, 132.5 (d, J_{PC} = 10 Hz), 131.5 (d, J_{PC} = 31 Hz), 131.1, 126.7, 126.5, 126.3 (d, J_{PC} = 13 Hz), 125.7, 34.7, 31.2; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 29.4; HRMS (FAB, *m*/*z*): calc. for $C_{54}H_{57}PO$, 753.4225; found, 753.4246. UV-vis: λ_{max} 335 nm (ε = 142 000 M^{-1} cm^{-1}). Calc. for $C_{54}H_{57}OP$: C, 86.13; H, 7.63. Found: C, 86.05, H, 7.48%.

MeTbs$_3$PI (3)

A solution of 0.300 g (0.407 mmol) of PTbs$_3$ and 0.116 g (0.814 mmol) MeI in 20 mL of anhydrous toluene was refluxed for 4 h. After cooling to room temperature, the product was filtered off, rinsed with *n*-pentane, and dried *in vacuo* to afford the phosphonium salt as a white powder (0.308 g, 86.2%): ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 27H), 3.16 (d, 3H, J_{HP} = 13 Hz), 7.08 (d, 3H, J = 16 Hz), 7.30 (d, 3H, J = 16 Hz), 7.41 (d, 6H, J = 8 Hz), 7.49 (d, 6H, J = 8 Hz), 7.73–7.77 (m, 12H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 20.0. HRMS (FAB, *m*/*z*, (M − I)$^+$): Calc. for $C_{55}H_{60}P$, 751.4433; found, 751.4434. UV-vis: λ_{max} 343 nm (ε = 87 800 M^{-1} cm^{-1}).

Cl$_2$PTbs$_3$ (4)

A solution of 0.300 g (0.407 mmol) PTbs$_3$ and 0.106 g (0.448 mmol) hexachloroethane in 25 mL anhydrous benzene was refluxed for 3 h. After cooling to room temperature, all volatiles were removed *in vacuo* and the crude solid was rinsed with anhydrous *n*-pentane, and dried *in vacuo* to afford 0.293 g (89.1%) of the product as an off-white powder: ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 27H), 7.06 (d, 3H, J = 16 Hz), 7.17 (d, 3H, J = 16 Hz), 7.30 (br d, 6H, J = 8 Hz), 7.41 (br d, 6H, J = 8 Hz), 7.48 (br, 6H), 7.68 (br, 6H). ^{31}P NMR ($CDCl_3$) δ 30.2. HRMS (FAB, *m*/*z*, (M − 2Cl + Na)$^+$): Calc. for $C_{54}H_{57}PNa$, 759.4096; found, 759.4081. UV-vis: λ_{max} 329 nm (ε = 103 000 M^{-1} cm^{-1}).

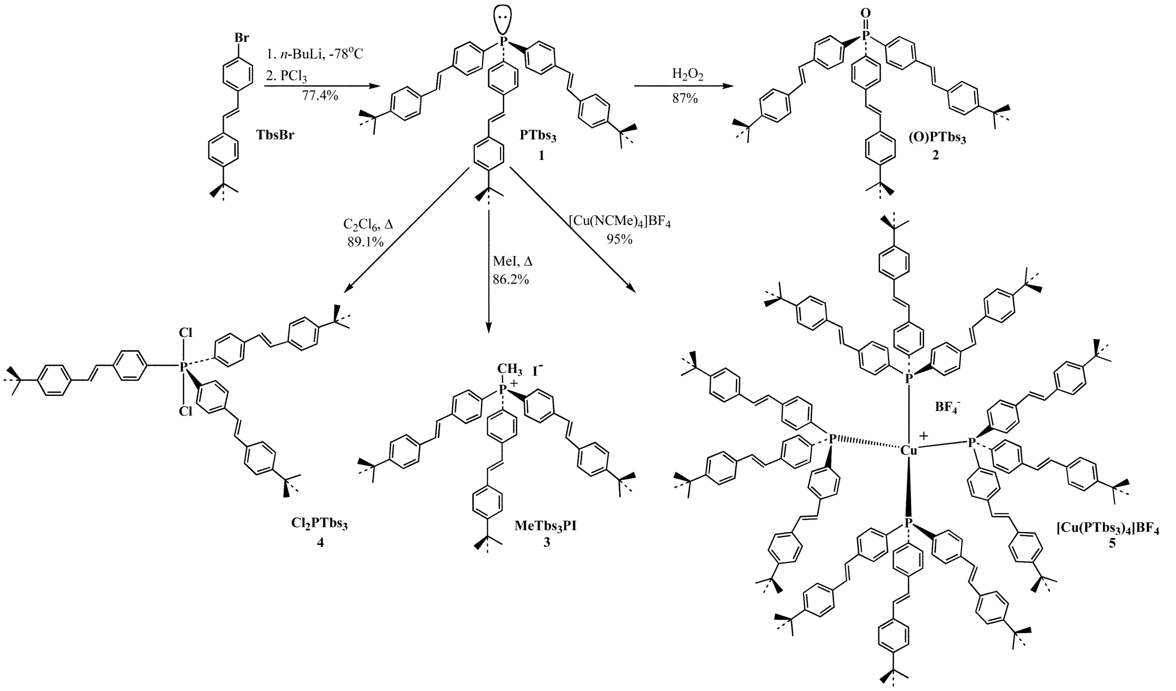
[Cu(PTbs$_3$)$_4$]BF$_4$ (5)

To a 50 mL round-bottom flask containing 20 mL dry CH_2Cl_2 was added 53 mg (0.17 mmol) [Cu(NCMe)$_4$]BF$_4$[13] and 500 mg (0.68 mmol) PTbs$_3$ with rapid stirring. After 1 h of stirring at room temperature all volatiles were removed *in vacuo* to afford **5** (500 mg, 95%) as a fine off-white powder. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 108H), 7.04 (d, 12H, J_{HH} = 16 Hz), 7.12 (d, 12H, J_{HH} = 16 Hz), 7.33–7.42 (m, 96H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.0, 138.7, 134.4 (d, J_{PC} = 16 Hz), 134.1, 132.0 (d, J_{PC} = 26 Hz), 129.8, 127.1, 126.5, 126.4 (d, J_{PC} = 11 Hz), 125.6, 34.6, 31.3; ^{31}P NMR ($CDCl_3$) δ 5.2. UV-vis: λ_{max} 332 nm (ε = 395,000 M^{-1} cm^{-1}).

Results and discussion

Synthesis

Tris(4-(4-*tert*-butylstyryl)phenyl)phosphine (PTbs$_3$), was prepared in 77.4% yield by the reaction of trichlorophosphine with the organolithium formed from TbsBr. The ^{31}P{^{1}H} NMR shift of δ −6.1 for **1** in solution differs by only about 1 ppm from that reported for PPh$_3$.[14] Compound **1** served as a convenient precursor to **2**–**5** by established methodologies (Scheme 1). Triarylphosphine oxide **2** was formed by reaction with hydrogen peroxide, phosphonium salt **3** by refluxing with MeI, and Cl$_2$PTbs$_3$ **4** by reaction with hexachloroethane.[15] The dendrimeric metal complex **5** was readily formed upon mixing of four equivalents of phosphine with [Cu(NCMe)$_4$]BF$_4$[13] in dichloromethane at room temperature. Successful formation of compounds was readily confirmed by high resolution mass spectroscopy. Multinuclear NMR spectroscopy (^{1}H, ^{13}C and ^{31}P) indicates the presence of a single species in all cases. The high resolution mass spectrum of **5**, however, did not show the M$^+$ peak corresponding to the proposed structure. Instead, the highest mass peak observed corresponds to a formulation of [Cu(PTbs$_3$)$_3$]-BF$_4$. Confidence in the assigned stoichiometry is thus derived from a number of additional checks. First, the reaction is nearly quantitative when the Cu salt and phosphine are mixed in a 1 : 4 ratio to produce a single species with new ^{1}H, ^{13}C and ^{31}P NMR resonances. Spiking an NMR sample of the complex with additional **1** leads to the appearance of additional resonances attributable to the free **1**. Finally, comparison of ^{1}H NMR peak integrations of **5** to those of an internal standard (1,4-dimethoxybenzene) also confirms the assigned ratio. Attempts to acquire accurate elemental analysis of **5** were unsuccessful, presumably due to the very hygroscopic nature of the material.



Scheme 1

Initial questions concerning the ability of the Cu center to accommodate four of the somewhat bulky phosphine ligands were also addressed by calculations to determine the optimized geometry of the complex (*vide infra*).

Structure

In addition to simply confirming the ability of the metal center in $[Cu(PTbs_3)_4]BF_4$ to accommodate four of the phosphine ligands, acquiring structural information for the complex would also help assess the viability of the material for practical applications. For example, the geometric arrangement of dipolar components is a critical factor in determining the utility of a material in NLO applications. Unfortunately, repeated efforts to grow X-ray quality crystals of $[Cu(PTbs_3)_4]BF_4$ have thus far been unsuccessful. Calculations at the PM3 level of theory (MacSpartan Plus, version 1.2.1), however, predict a fascinating “supermolecular tetrahedron” (Fig. 1). Such an arrangement is formed as three stilbene moieties, one from each phosphine on a face of a CuP_4 tetrahedral dendrimer core, are intertwined to form each of the four protrusions. Steric clashes between the stilbene moieties about adjacent phosphines appear to drive the formation of such a conformation. This geometry may be further stabilized by π–π stacking between adjacent stilbene units in each strand. Such a supermolecular tetrahedron places three terminal *tert*-butyl groups at each corner with the metal charge isolated in the center, creating an arrangement of dipoles appropriate for the type of quadrupolar NLO properties that are of current interest.[5] From a structural standpoint, the ability to distribute 12 dipolar units in such a way is anticipated to lead to more striking effects than those exhibited by other tetrahedral systems such as **A** (Chart 1, four dipolar units). Such properties could conceivably be further enhanced by replacement of *tert*-butyl groups with more strongly donating groups to create a stronger set of dipoles. Current work is underway to construct such systems.

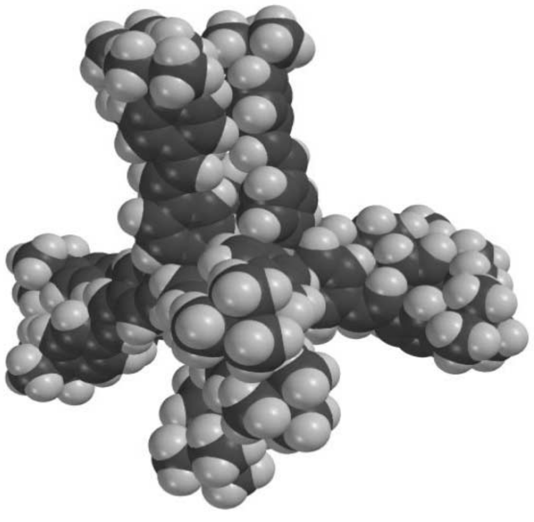


Fig. 1 Calculated structure of $[Cu(PTbs_3)_4]BF_4$.

Spectroscopy

Fig. 2 shows the absorption (top) and fluorescence (bottom) spectra for the series of compounds **1**–**5**. The absorptivity and fluorescence intensity have been normalized to intensity per mole of stilbenyl units to facilitate direct comparison. The spectra for the model compound (*E*)-4-methyl-4′-*tert*-butylstilbene (**6**) are also shown for comparison. This material was chosen because it represents a single chromophore hydrocarbon with approximately the same morphology as the stilbenyl subunits of which **1**–**5** are composed. As such, this model is expected to approximate the properties that would be exhibited by **1**–**5** in the absence of heavy atom or lone pair effects, or intramolecular chromophore–chromophore interactions, all of which may impact photophysical properties.

The absorptivity per stilbenyl is fairly constant for the entire series, with all compounds having an absorptivity slightly lower than that of **6**. The absorption maxima ($\lambda_{\pi-\pi^*}$) for **1**–**5** are all slightly red shifted with respect to **6**, indicating that some degree of conjugation with or across the phosphorus center may be taking place. The extent of conjugation is less dramatic than that observed for the interaction of nitrogen with aromatic systems (the “amino conjugation effect”).[16] The diminished interaction with phosphorus is to be anticipated, as a conjugative interaction requires phosphorus to acquire a planar conformation and formal sp^2 hybridization, a much less favorable process for heavier main group elements.[17]

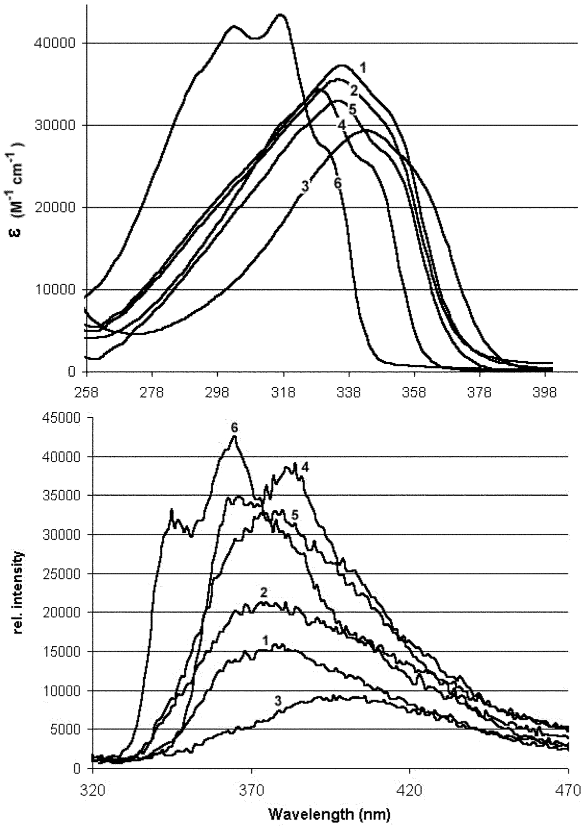


Fig. 2 Absorption (top) and fluorescence (bottom) spectra for compounds **1**–**6** ($CHCl_3$, per mole of stilbenyl moiety).

In contrast to absorptivity, the fluorescence intensity per stilbenyl unit varies greatly across the series. The variation of fluorescence intensity with coordination number or geometry in trianthryl phosphorus compounds revealed that the extent to which adjacent fluorophores interact most influences the luminescence.[10] Close contact of adjacent fluorophores may allow nonradiative internal quenching by exiton transfer, for example. Such interactions were anticipated to be reduced here, as the stilbenyl fluorophores employed have considerably less lateral extension than anthryl groups. Indeed, the trend seen in Fig. 2 (bottom) suggests that the phosphorus lone pair may be responsible for fluorescence quenching in the current case. The involvement of the phosphorus lone pair in nonradiative decay pathways has previously been presented as an explanation for diminished fluorescence.[18] This conclusion is supported by the observation that the fluorescence intensity of Cl_2PTbs_3, $[Cu(PTbs_3)_4]BF_4$ and $O{=}PTbs_3$ are all significantly enhanced *vs.* $PTbs_3$ in which the lone pair is unbound. The notably lower fluorescence in $MeTbs_3PI$ may indicate that the iodide counterion, a well documented fluorescence quencher, decreases luminescence. It should also be noted that although the proposed geometry of $[Cu(PTbs_3)_4]BF_4$ (Fig. 1) places adjacent stilbenyl fluorophores in close proximity to one another, the relative fluorescence is not significantly diminished. In fact, the fluorescence intensity of **5** is only slightly less per stilbenyl moiety than that of Cl_2PTbs_3, in which the stilbenyl units are maximally disposed. This may be at least partially attributed to the utility of bulky *tert*-butyl groups that prevent close face-to-face interactions of adjacent π systems.

Conclusion

In conclusion, a series of new phosphorus-(III) and -(V) compounds featuring stilbenyl ligands in various geometries, as well as a dendrimeric Cu(I) complex, have been prepared. While absorption spectra show no striking changes with geometry or coordination number, fluorescence intensities vary. The observed fluctuation in fluorescence seems to indicate that the phosphorus lone pair contributes to fluorescence quenching. Calculations indicate that the Cu(I) complex displays an interesting “supermolecular tetrahedron” geometry with an arrangement of dipoles appropriate for nonlinear optical systems. Current efforts are underway to confirm this geometry and to apply the initial findings presented herein to the rational design of related systems with specific optical and structural properties.

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