Blue/Red Linear Dichroic Emission from a Highly Anisotropic Crystal of Triarylmethane Dye Conjugated with Phenoxo-Zinc Complexes

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Chem. Eur. J. 2011, 17, 1122-1127

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Abstract: We have developed a novel triphenylmethane-based hexanuclear zinc complex that exhibits peculiar photochemical and photophysical properties. Upon UV irradiation, the compound turned from colorless to reddish purple, while the color of emission turned from blue to red. The color change was attributed to an oxidation of the ligand part. It was suggested that an intramolecular energy-transfer mechanism operates to give rise to the red emission. The UV treatment of a

Keywords: crystal engineering • energy transfer • luminescence • polarized emission • transition metals

single crystal results in simultaneous emission of orthogonally polarized blue and red light. This color switching, namely linear dichroic emission was so distinct that one can recognize with by sight through optical microscope. The columnar arrangement of molecules in the crystal clearly accounts for the observed polarization of the emission.

Introduction

Organic molecules with multiple emission modes in the visible region have recently attracted a great deal attention, largely because they are promising candidates as chromophores in white-light emitting devices, displays, computer memories, switches in wave optics, chemical sensing probes, and so forth.^[1] Thus far, several attempts have been made to create such molecules with efficient emission over multiple modes. Although solid-state luminescence is more interesting and useful for industrial applications, various intra- and intermolecular interactions in the condensed phase often result in diminished emission efficiency. Crystal packing or aggregation pattern can play a decisive role in controlling solid-state luminescence,^[2] which is probably related to the mutual arrangement of the transition moment vectors of the chromophores.

A highly axle-symmetric molecule with a rigid core can be a useful building unit that forces functional moieties to have a preferred arrangement in solid state.^[3] Triarylmethane (TAM) derivatives meeting this prerequisite have been extensively studied and applied to supramolecular complexes,^[4] nano-scale fibers,^[5] self-assembled monolayers,^[6] and liquid crystals.^[7] Furthermore, it is interesting that the "leuco" form of TAM suffers oxidative dissociation by photoirradiation, releasing hydride, hydroxide, or cyanide from the central carbon atom.^[8] As a result, a virtually planar methylium π -system is responsible for the vivid colors of synthetic dyes such as crystal violet.^[9] By virtue of this interesting property, a variety of TAMs with different aryl groups, including heteroaromatic rings, were devel-

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oped^[10] and applied to a variety of functional dyes, including nonlinear optical materials and near-infrared dyes.[11-14] Also, the combinations with various inorganic materials lead to new functions utilizing the intrinsic electronic properties of TAM and the related dye compounds.^[15] However, there have been few studies on well-defined metal complexes assembled with a TAM core. In this paper, we will present a novel triangular triphenylmethane derivative that has µ-phenoxo-bridged dinuclear zinc moieties at each apex. This C_3 symmetric hexanuclear Zn complex was crystallized in hexagonal rods and exhibited interesting photoproperties, including UV-induced color change and blue/red bimodal emissions with orthogonal polarization planes. We describe herein the relationship between the molecular structure, crystal packing, and spectroscopic properties of this material.

Results and Discussion

Compound 1H₃ was synthesized from 4,4',4"-trihydroxytriphenylmethane by converting the phenol groups into 2,6-bis-(*N*,*N*-bis(2-pyridylmethyl)aminomethyl)phenol (bpmpH) units. Subsequently, 1H₃ was complexed with zinc acetate (Scheme 1, further details are available in the Supporting Information). Addition of PF_6^- or BF_4^- ions to the solution of $[Zn_61(OAc)_6]^{3+}$ in methanol led, in both cases, to the formation of a hexagonal crystalline solid precipitate. The crystalline precipitate was colorless to slightly pink in color. Although the ¹H NMR spectrum showed a series of broadened peaks in the methylene region, comparison with the spectrum of a model compound shows that every methylene proton couples with its geminal counterpart (Figure S1 in the Supporting Information). This observation suggests a suppressed intramolecular motion due to the rigidity and steric hindrance of the molecular framework.

We obtained a single crystal of $[Zn_61(OAc)_6][BF_4]_3$ suitable for X-ray crystal-structure analysis (Figure 1). The central methine carbon of $[Zn_61(OAc)_6]^{3+}$ unit lies on the crystallographic *c* axis, and one third of the unit is crystallographically independent. There are two more independent $[Zn_61(OAc)_6]^{3+}$ units in the crystal, although the structure of these three are essentially same. The structure of each $[Zn_2(bpmp)]^+$ unit was similar to those reported for analo-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002950.



[Zn₆1(OAc)₆]³⁺

Scheme 1. Synthesis and structure of the triphenylmethane-based hexanuclear complex. i) dimethylamine, paraformaldehyde, reflux in MeOH, 30 min; ii) bis(2-pyridylmethyl)amine, liquid paraffin, 130 °C, 30 h; iii) zinc acetate dihydrate, MeOH.

gous dinuclear complexes.^[16] The central methine carbon adopts a considerably flattened pyramidal structure (angles of H-C(methine)-C(phenyl) are 103.3, 105.0, and 105.3°), probably due to steric repulsion among the [Zn₂(bpmp)]⁺ units.

A single crystal of $[Zn_61(OAc)_6](BF_4)_3$ (ca. $10 \times 10 \times$ 100 µm³ in size) was set in an optical microscope and irradiated with a high-pressure Hg lamp (100 W, $380 > \lambda >$ 330 nm). At the beginning of the irradiation, the crystal exhibited a blue emission, but as time elapsed, the emission turned a reddish orange through reddish purple. Moreover, we found that the emission was a mixture of blue and red rays that were orthogonally polarized (Figure 2). Simultaneous with the emission change, the crystal turned reddish purple.

The emission spectra ($\lambda > 420 \text{ nm}$) of the single crystal were measured by varying the transmission axis of the analyzer relative to the crystallographic c axis (Figure S2 in the Supporting Information). The spectra measured under conditions in which the transmission is parallel to the c axis (cparallel) showed an emission band with the highest peak at 490 nm, which weakened as time elapsed. The spectra measured under conditions in which the transmission is perpendicular to the c axis (c-perpendicular) showed a bimodal band with emission maxima at 460 and 620 nm. A sharp depression around 550 nm is attributable to re-absorption due



Figure 1. Crystal structure of [Zn₆1(OAc)₆][BF₄]₃. Top: A representative hexanuclear unit. Bottom: the crystal packing viewed along the c axis. In bottom view the methine carbon atom and its surroundings are shown in pink. The zinc atoms and its surroundings are shown as gray polyhedra.



Figure 2. Optical micrographs of a single crystal of [Zn₄1(OAc)₄][BF₄] after UV irradiation for about 5 min. The emission images shown in a) and b) were taken using parallel and perpendicular positions, respectively, of the analyzer transmission axis. The transmission images shown in c) and d) are of the same sample observed using parallel and perpendicular polarizer positions, respectively.

to a photoproduct (vide infra). The emission at 460 nm decreased more rapidly as time elapsed and corresponded to a relative increase of emission at 620 nm. Namely, the photoproduct has an emission around 620 nm, which compensates

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for the decrease of the original emission. The spectral changes seemed saturated within an irradiation time of 32 min (Figure S2 in the Supporting Information), and we confirmed by microscopic observation that the crystal hardly collapsed during this period. The spectra of the saturated state strongly showed linear dichroism in the emission (Figure 3). No such distinct blue/red switching has been reported so far in studies of dichroic emission or polarized emission.^[17]



Figure 3. Top: Emission spectra of a single crystal of $[Zn_61(OAc)_6][BF_4]_3$ after 32 min of UV irradiation measured with the analyzer at *c*-parallel (solid line) and at *c*-perpendicular (dashed line) positions. Bottom: Optical micrographs of the single crystal corresponding to the above conditions.

As can be seen from Figure 2c and d, the degree of absorption is also strikingly dependent on the polarization plane of the incident light. We measured absorption spectra of a single crystal of $[Zn_61(OAc)_6][BF_4]_3$ and confirmed that the transmission axis coincides with the crystallographic *c* axis (Figure S3 in the Supporting Information). By comparison of the above results with the crystal structure, it is evident that the observed linear dichroic emission and absorption are related to the TAM framework stacked along the *c* axis. We assume that the chromophore of the photoproduct has transition dipoles parallel to the *a* and *b* axes, implying that an extended π -conjugated system was formed in the plane perpendicular to the *c* axis. We observed similar photoluminescence behavior for $[Zn_61(OAc)_6][PF_6]_3$ (Figure S4 in the Supporting Information), though the crystal thickness was insufficient for measurement of single-crystal emission spectra. To elucidate the origin of the photoinduced color change, we allowed the PF_6 salt to turn reddish orange by prolonged UV irradiation. The absorption spectra of the photoproduct in solution (CH₂Cl₂, 1×10^{-4} M) showed a peak around 540 nm, which was not observed for the sample before irradiation (Figure 4, top). This band has a shapeless profile, typical of



Figure 4. Top: Absorption spectra of $[Zn_61(OAc)_6](PF_6)_3$ before radiation (dashed line) and after UV irradiation (solid line). Absorption spectra of aurin under basic conditions (MeOH, 1×10^{-5} M; dotted line). Bottom: Fluorescence spectra (solid lines: $(\Box) \lambda_{ex} = 350$ nm, (**u**) $\lambda_{ex} = 500$ nm) and excitation spectra (dashed lines: $(\Box) \lambda_{em} = 448$ nm, (**u**) $\lambda_{em} = 578$ nm) of the UV-irradiated sample of $[Zn_61(OAc)_6](PF_6)_3$.

TAM-based dyes.^[9] It is instructive to compare the observed absorption spectra (Figure 4, top) with that of aurin (1,4-benzoquinone-bis(4-hydroxyphenyl)methide) under basic conditions (Scheme S1 in the Supporting Information). The intense absorption around 540 nm is attributed to the ${}^{1}A_{1} \rightarrow {}^{1}E$ transition, which has two transition dipoles in the π -conjugated plane.^[9] Apparent similarity between these spectra suggests that the photoproduct involves an oxidized quinoidal form, such as $[Zn_{6}2(OAc)_{6}]^{4+}$ (Scheme 2). Based on the ratio of absorbance (1:7), we estimate the gross ratio of photo-conversion to be 10-20%. Since the extremely flattened pyramidal structure around the central methine carbon atom (Figure 1, top) suggests a predisposition for aromatization, this photoreaction does not cause serious strain in the crystal lattice.

Fluorescence and excitation spectra were also measured for the UV-irradiated sample of $[Zn_61(OAc)_6](PF_6)_3$ in solution (CH₂Cl₂, 1×10⁻⁴ M). Upon excitation at 350 nm, we ob-

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[Zn₆2(OAc)₆]⁴⁺

Scheme 2. Structure of the oxidized form of the TAM-based complex.

served an intense emission band with a peak at 448 nm, accompanied by a weak band around 570 nm (Figure 4, bottom). Note that the weak band around 570 nm was completely absent in the spectrum of the non-irradiated sample (Figure S5 in the Supporting Information). An excitation spectrum for the emission at 448 nm shows two peaks at 320 and 370 nm, which are roughly in agreement with the absorption maxima of $[Zn_61(OAc)_6][PF_6]_3$, while the intensity at 370 nm is prominently higher in the excitation spectrum. On the other hand, the excitation spectrum for the emission at 578 nm shows an intense peak at 548 nm, while the aforementioned peaks around 320 and 370 nm are relatively small. The profile around 548 nm is quite similar to the absorption band of aurin, suggesting that the newly appeared emission around 570 nm is attributable to the oxidized quinoidal form of $[Zn_61(OAc)_6]^{3+}$. As expected, altering the excitation wavelength to 500 nm resulted in the observation of an intense emission band with a peak at 578 nm. Note that aurin itself does not fluoresce either in solution or in the solid state due to vibrational energy loss from fluctuation of the phenyl rings. The weak but observable emission from the aurin core in the complex may have resulted from the bulkiness of the chelating moiety that suppresses the intramolecular motion. From the excitation spectra described above, we conclude that irradiation at 330 nm can cause emission at 578 nm through a partial energy transfer from the peripheral zinc complex units to the central aurin-like moiety.

It is possible that a similar process occurs in the crystalline state. Namely, irradiation of UV light causes electronic excitation in the $[Zn_2(bpmp)]^+$ units which emit at 490 nm. Simultaneously, partial energy transfer occurs between the complex units to the aurin-like moiety in the photo-oxidized species. In addition, re-absorption of the emitted light by the aurin-like moiety is implied from the sharp depression around 540 nm in the emission spectra observed for the $[Zn_61(OAc)_6](BF_4)_3$ crystal under *c*-perpendicular conditions (Figure 3, bottom). The aurin-like core then emits at 600 nm corresponding to ${}^{1}E \rightarrow {}^{1}A_1$ transition, for which the transition dipoles are perpendicular to the *c* axis. This proposed mechanism accounts for the linear dichroic emission observed for the hexagonal crystals of $[Zn_61(OAc)_6][BF_4]_3$ and $[Zn_61-(OAc)_6][PF_6]_3$ (Figure 5).



Figure 5. Schematic representation of the linear dichroic emission of the $[Zn_{62}(OAc)_6]_4^+$ in the $[Zn_{61}(OAc)_6]X_3$ crystal.

Conclusion

In summary, we have developed a novel conjugated dye molecule composed of a TAM unit and µ-phenoxo-bridged dinuclear zinc complex that shows a clear linear dichroic emission. The symmetric structure and rigidity of the molecular framework allows for crystallization of the compound in a hexagonal columnar fashion with a highly anisotropic molecular arrangement. The molecule in the "leuco" form undergoes oxidation to the "dye" form by UV irradiation and then shows blue/red dual emissions that have perpendicular polarization planes. By changing the direction of the dichroic filter, the blue/red switching is so distinct that it is recognizable with the naked-eye. We attribute the red emission to the central aurin-like moiety and intra- and intermolecular energy-transfer mechanisms that effectively distribute the polarized light with different wavelength. In this system, the photophysical property of aurin, which is normally non-fluorescent, was modified by embedding it in more favorable molecular surroundings. This study clearly demonstrates that appropriate molecular design can lead to the development of new materials with unique properties that originate from the molecular arrangement.

Experimental Section

Spectroscopic measurements: The absorption and luminescent spectra of a single crystal was measured by using a conventional polarized optical microscope (Olympus, BX-51) equipped with an optical fiber that was connected to a spectrometer (Ocean Optics, USB4000). For absorption spectra, a halogen lamp was used as a light source, and the transmission with wavelength of 400–800 nm was detected. For luminescent spectra, high pressure Hg lamp (output 100 W) was employed with a band-pass

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filter for wavelength of 330–380 nm, and the emission with wavelength of > 420 nm was detected.

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Received: October 13, 2010