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Magnetic Circular Dichroism of Luminescent Triarylmethyl Radicals

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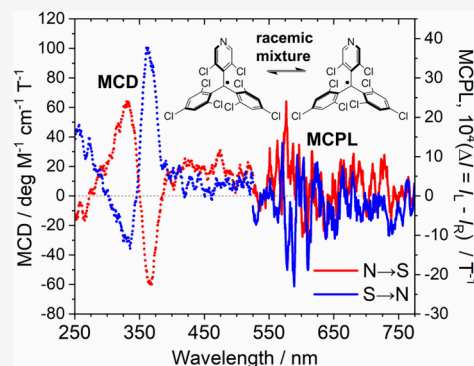
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ABSTRACT: Stable triarylmethyl radicals are the most common carbon radical building blocks and have recently attracted much attention for their luminescent properties. However, magnetic circular dichroism (MCD) discovered by Michael Faraday and magnetic circularly polarized luminescence (MCPL) have not been observed for simple triarylmethyl radicals, probably due to their photodegradability. Here we report the first observation of MCD and MCPL of triarylmethyl radicals in solution using racemic mixtures of (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM) and (3,5-difluoro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (F₂PyBTM), which are much more photostable than simple triphenylmethyl radical derivatives. Faraday *B* terms, which are at the origin of magnetic dichroism in nondegenerate systems, were calculated using TD-DFT, and the line shape of MCD spectra was well reproduced. This study provides new circular dichroism properties for luminescent triarylmethyl radicals in solution without separating enantiomers and also clarifies the origin of magnetic circular dichroism properties of stable organic radicals for the first time.



Triarylmethyl radicals protected by halogen atoms are the most common form of stable carbon radical.¹ Three aryl rings are conjugated to the central α -carbon but tilted with respect to the sp^2 plane with the radical center for steric reasons. Thus, the shapes of these radicals are typically propeller-like.

One of the features commonly found in these radicals is luminescence.² The emission of these radicals is unique compared to that of common closed-shell molecules in that it is a fluorescence from the doublet excited state to the doublet ground state. Spin-multiplicity is particularly important for applications in electroluminescence (EL), and an efficient organic light-emitting diode (OLED) has been obtained.³ Unlike the lowest triplet excited state in the closed-shell molecules, there are no spin-forbidden excited states lower than the lowest spin-allowed excited state. Unique photo-physical properties such as the specific heavy-atom effect^{4,5} and magnetic-field effect on luminescence (magnetoluminescence)^{6,7} are also observed.

In 2019, Veciana and co-workers separated the left- and right-handed enantiomers of propeller-like triarylmethyl radicals (Figure 1), tris(2,4,6-trichlorophenyl)methyl radical (TTM)⁸ and perchlorotriphenylmethyl radical (PTM)^{9,10} by using chiral stationary phase (CSP) HPLC.¹¹ They first reported electronic circular dichroism (ECD) and circularly polarized luminescence (CPL) of both (*P*- and (*M*-enantiomers of these radicals at -20 °C, since they racemize at room temperature with a racemization barrier of 20 kcal mol⁻¹. They also prepared the tris(2,4,6-tribromophenyl)-

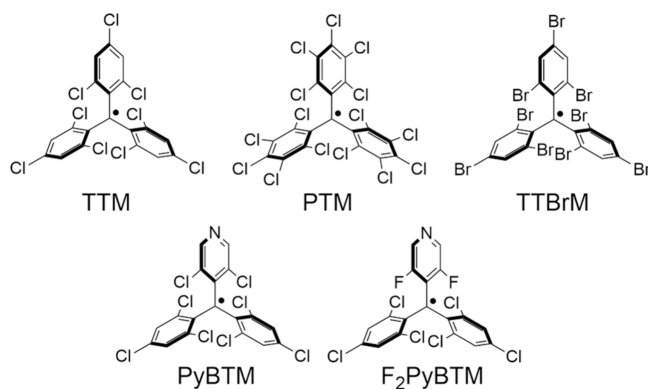


Figure 1. Structures of the (*P*-enantiomers of TTM, PTM, TTBrM, PyBTM and F₂PyBTM.

methyl radical (TTBrM) without any racemization up to 60 °C.¹²

To observe circular dichroism, CSP-HPLC is an expensive option, and subsequent racemization is still a major problem for most triarylmethyl radicals. Circular dichroism of symmetric materials induced by a longitudinal external

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magnetic field was discovered by Michael Faraday,¹³ and MCD of organic π -systems such as porphyrins, phthalocyanines,¹⁴ and heme proteins¹⁵ has been used to study the electronic structures. Circular dichroism in luminescence under longitudinal external magnetic field, called MCPL, is also observed for many basic luminescent organic molecules.¹⁶ In this paper, we describe the MCD and MCPL of simple triarylmethyl radicals in organic solution at room temperature and discuss their origins.

In this study, we used triarylmethyl radicals, PyBTM¹⁷ and F₂PyBTM,¹⁸ for the measurements of MCD and MCPL. Their absorption and emission properties resemble those of TTM and PTM, which are persistent radicals in the dark but decompose quickly under photoirradiation.¹⁹ PyBTM and F₂PyBTM are much more (>70 times) photostable than TTM in dichloromethane and therefore suitable for optical measurements. PyBTM has also been used for some photophysical measurements such as the coherent coupling between spin ensembles²⁰ and photoluminescence anisotropy amplified by exciton funneling.²¹

MCD spectra of the triarylmethyl radicals in dichloromethane were measured by using a JASCO J-820 circular dichroism spectrometer with a 0.8 T permanent magnet (Figure 2). As a result of 32 times accumulation of

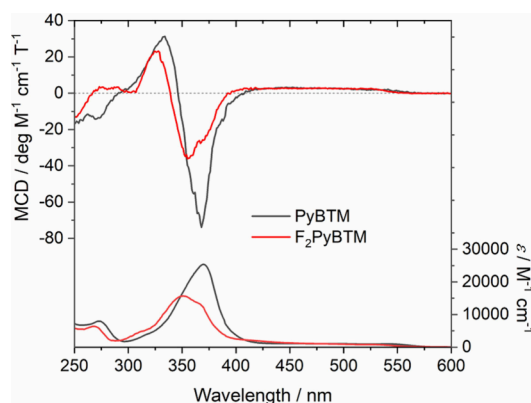


Figure 2. MCD spectra of PyBTM (in black, 1.3×10^{-3} M (250–330, 390–420 nm), 5.6×10^{-4} M (330–390 nm), 8.0×10^{-3} M (420–600 nm)) and F₂PyBTM (in red, 1.1×10^{-3} M (250–330, 380–420 nm), 5.9×10^{-4} M (330–380 nm), 9.7×10^{-3} M (420–600 nm)) in dichloromethane under 0.8 T (N-up). Absorption coefficients are shown at the bottom.

measurements with concentrated solution ($\sim 1 \times 10^{-3}$ M), the visible absorption bands of PyBTM and F₂PyBTM (550–425 nm) showed weak positive MCD. PyBTM indicated a negative MCD peak at 368 nm and a positive MCD peak at 334 nm. F₂PyBTM showed a smaller negative MCD signal at 355 nm and a positive signal at 328 nm. The positions of the negative peaks were near the absorption maxima of PyBTM and F₂PyBTM at 370 and 351 nm, respectively.

The intensity of MCD depends on Faraday A, B, and C terms, although only the B term is involved in a nondegenerate electronic system.¹³ The B term from ground electronic state m to excited electronic state n is given by^{22–24}

$$B_{nm} = \sum_{k \neq n} B_{nm}^{(k)} \quad (1)$$

$$B_{nm}^{(k)} = \text{Im} \left\{ \frac{\mathbf{M}_{nk} \cdot (\boldsymbol{\mu}_{nm} \times \boldsymbol{\mu}_{km})}{E_k - E_n} \right\} \quad (2)$$

where $E_k - E_n$ is the energy difference between excited states k and n , \mathbf{M}_{nk} is the magnetic dipole moment between excited states, and $\boldsymbol{\mu}_{nm}$ and $\boldsymbol{\mu}_{km}$ are the electric dipole moments between excited and ground states. The MCD spectrum can be calculated from^{22–24}

$$\Delta \varepsilon(\omega) \propto -\omega B_{nm} f(\omega) \quad (3)$$

where ω is the photon frequency and $f(\omega)$ is the line shape function, which was expressed by the Gaussian function in this study.

The ground and excited electronic structures of PyBTM and F₂PyBTM, which had C₂ symmetry at the ground state, were calculated at the M06-2X/6-31G(d,p) and TD-M06-2X/6-31G(d,p)²⁵ functionals within the Tamm-Dancoff approximation, respectively. The solvent effect of dichloromethane was considered using a polarizable continuum model (PCM).^{26,27} We note that the M06-2X functional well reproduced the absorption spectral line shape of PyBTM in both the visible and near-UV regions, compared to the B3LYP functional (Figure S1). The electronic structure was computed using Gaussian 16 Revision C.01.²⁸ Magnetic and electric dipole moments were computed using MultiWfn 3.8.²⁹ The active space of the excited states was taken from D₁ to D₅₀.

The DFT calculations attributed the weak visible absorption band of PyBTM and F₂PyBTM to D₀ → D₁, which mainly consisted of the β -HOMO → β -LUMO transition for PyBTM and the β -HOMO-1 → β -LUMO transition for F₂PyBTM (Figure 3, Tables S1–S2).^{17,18} This transition had a small

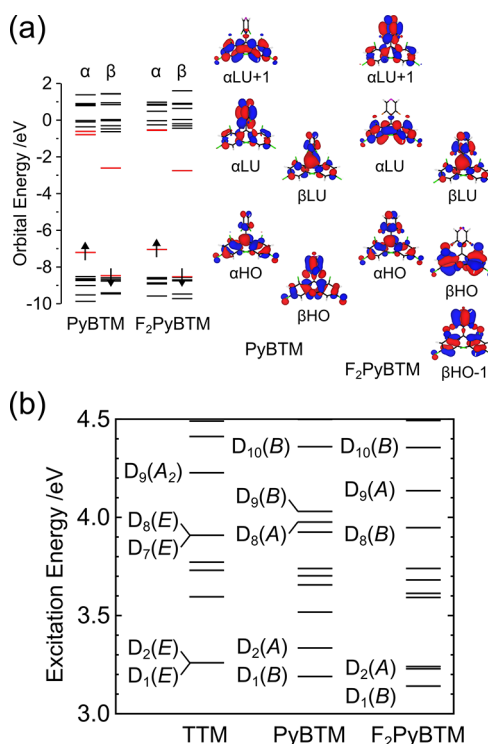


Figure 3. (a) Calculated orbital levels and molecular orbitals (isosurface value: 3×10^{-2} a.u.) of PyBTM and F₂PyBTM at the D₀ optimized structure. (b) Calculated energy levels of excited states for TTM, PyBTM, and F₂PyBTM at the D₀ optimized structure.

oscillator strength due to the nearly 3-fold molecular symmetry.³⁰ The strong near-UV absorption bands were attributed to $D_0 \rightarrow D_8$ and $D_0 \rightarrow D_9$, which mainly consisted of the transitions from the α -HOMO to the pseudodegenerate α -LUMO and α -LUMO+1 (Figure 3a, Tables S1–S2).

The calculated MCD spectra of PyBTM and F₂PyBTM well reproduced the line shape of the experimental spectrum (Figure 4). The B terms of D₈ and D₉, which contributed to

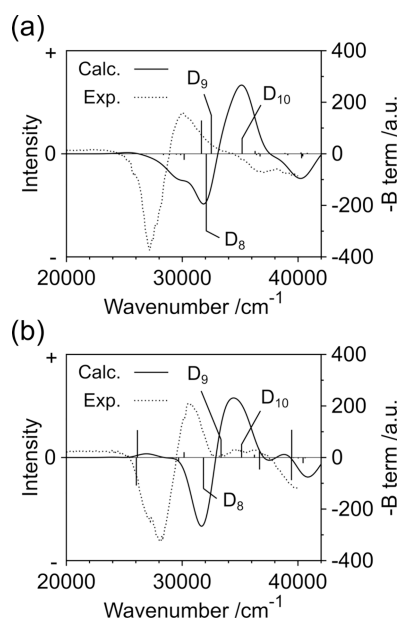


Figure 4. Calculated N-up MCD spectra of (a) PyBTM and (b) F₂PyBTM with a line width of the Gaussian function 1000 cm⁻¹. Vertical lines represent the Faraday B terms.

the negative and positive MCD, respectively, were large. This was attributed to the large electric transition dipole moments of $D_0 \rightarrow D_8$ and $D_0 \rightarrow D_9$ and strong magnetically induced mixing between D₈ and D₉ (Tables S3–S4). The strong mixing arose from the pseudodegeneracy of D₈ and D₉, i.e., energetically close excited states, which originated from the symmetry breaking of degenerate D₇ and D₈ of TTM with D₃ symmetry (Figure 3b, organic molecules with degeneracy show strong MCD^{13–15}). The B term of D₁₀, which corresponded to D₉ of TTM, also contributed to the positive MCD because of the mixing with D₈ and D₉ (Tables S3–S4). Thus, it was found that the strong MCD was induced by the optical absorption into the pseudodegenerate excited states with large electric dipole moments to the ground state.

On the other hand, the B terms in the visible region were small except for a few excited states (Figure 4 and Figure S2). The slight negative value of the B term of D₁ is consistent with the experimental results, but the accuracy of calculations for small values cannot be guaranteed. The B term of D₁ mainly originated from the mixing with the energetically high-excited states having large electric dipole moments (Tables S3–S4).

MCPL spectra of the triarylmethyl radicals in dichloromethane were measured using a JASCO CPL-300 spectrometer with a 1.7 T permanent magnet (Figure 5). MCD spectra measured using a JASCO J-1700 Circular Dichroism spectrometer with the same magnet are shown in Figure S3. Although the MCD signal of the D₁ excited state absorption was very weak, positive MCPL signals were shown when Faraday-type N \rightarrow S (N-up) geometry was employed, and

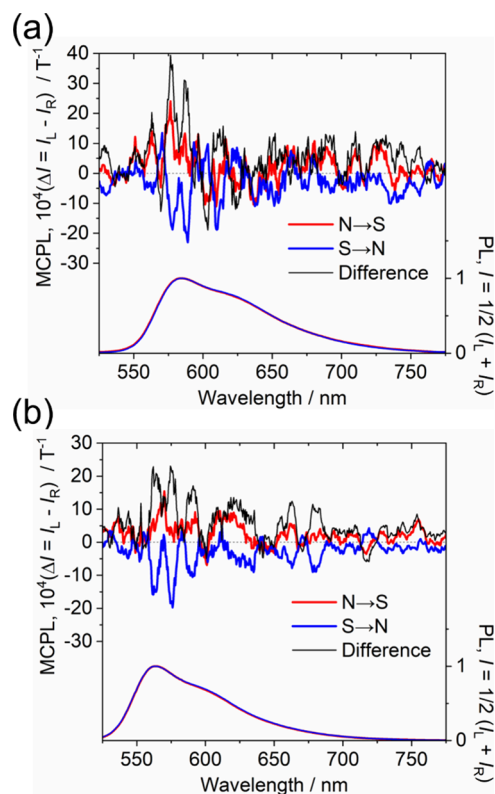


Figure 5. MCPL spectra of (a) PyBTM and (b) F₂PyBTM in dichloromethane (1.0×10^{-3} M) under N-up (red lines) and S-up (blue lines) Faraday geometry under 1.7 T. I_L and I_R are the intensities of the left- and right-handed MCPL, respectively. Photoluminescence spectra under a magnetic field are shown at the bottom.

negative MCPL signals were shown when Faraday-type S \rightarrow N (S-up) geometry was employed. The noises in the spectra could not be eliminated due to the small fluorescence quantum yields of PyBTM ($\Phi_f = 2\%$) and F₂PyBTM ($\Phi_f = 4\%$) and the limited number of accumulations due to the photodegradation by the strong excitation light. Also, the spectral line shapes of MCPL in the visible region might be attributed to the vibronic progressions,³¹ and these effects need to be considered for detailed discussion. Although the line shape is unclear, it is important to note that the sign of the signal was reproducible after repeated similar experiments (Figure S4). The magnet of the CD spectrometer (Figure 1) was fixed to N-up and the sign of MCD corresponding to the D₁ excited state (weak visible band) agreed with the sign of MCPL. The Faraday B terms of $D_0 \rightarrow D_1$ and $D_1 \rightarrow D_0$ are small but certainly present. Importantly, CPL was observed without separating the enantiomers.

Electron-donor substituents are known to drastically increase the photoluminescence quantum yield of triarylmethyl radicals. For such brightly luminescent donor-radical acceptor systems, CPL properties were induced by a magnetic field, supramolecular assembly and chiral liquid crystal encapsulation.³² A chiral donor-radical acceptor system using pillar[5]-arene was reported to exhibit CPL.³³

We also tried to measure MCPL spectra of some donor-PyBTM systems such as Mes₂F₂PyBTM³⁴ and the donor-bridged diradical system PyBTM-(Hex₂Ph)PyBTM;³⁵ however, MCPL in solution was not detected similarly to donor-TTM or donor-PTM systems in hexane solution.³² It is

plausible that the rotation of the single bond between the donor and the radical cancels out the CPL properties in solution.

In conclusion, MCD and MCPL of simple triarylmethyl radicals were observed for the first time in solution, and the signals were explained by Faraday *B* terms calculated using DFT. The MCD signal arising from the α -HOMO to the pseudodegenerate α -LUMO and α -LUMO+1 transitions has the potential to give information on the electronic symmetry of these radicals. The ability to induce CPL using only a magnetic field, without requiring enantioenriched samples, opens up new possibilities for luminescent radicals, which are unique as magnetic organic molecules.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.4c02793>.

Calculated absorption spectra and Faraday *B* terms, MCD and MCPL spectra under 1.7 T, TD-DFT data tables (PDF)

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Notes

The authors declare no competing financial interest.

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