Deep-red circularly polarized luminescent C70 derivatives

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Article

Keywords: fullerenes, photoexcited chirality, X70A, bis-borylated xanthene, chiral-HPLC, nanocarbon materials

Posted Date: July 22nd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-40543/v1>

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Abstract

Optically active fullerenes (C₇₆, C₈₂, C₈₄), including C₆₀ and C₇₀ derivatives carrying organic substituents, possess various potent applications because of unique spectroscopic, catalytic, and chiral recognition properties. However, their inherent photoexcited chirality has not yet been elucidated because of a very poor quantum yield of fluorescence (FL). With this background in mind, we synthesized new chiral C₇₀ derivatives, X70A, solely by reacting bis-borylated xanthene with C₇₀ in a one-step double addition reaction with 20% yield, followed by a successful optical resolution using a recyclable chiral-HPLC technique. The isolated X70A enantiomers were confirmed by their mirror-image circular dichroism spectra in the range of 300 nm and 700 nm. The enantiomeric pair of X70A in toluene revealed clearly mirror-image circularly polarized luminescence (CPL) spectra with a high $|g_{\text{lum}}|$ value of 7.0×10^{-3} at 690 nm associated with FL lifetime of 0.99 ns. The deep-red CPL of X70A should provide new photofunctionality as chiral nanocarbon materials.

Introduction

Achiral buckminsterfullerene (C₆₀) and [5,6]-fullerene (C₇₀) adopt highly symmetrical spherical and elliptical structures, respectively, allowing utilizing as *n*-type molecular semiconductors and building blocks of molecular conductors/magnets owing to the uniqueness of energetically low-lying lowest unoccupied molecular orbital (LUMO)^{1,2}. Actually, the LUMO characteristics of C₆₀ and C₇₀ in solutions permit to reversibly accept and release up to six electrons by electrochemical redox process³. Also, K₃C₆₀⁴ and Rb₃C₆₀⁵ reveal superconductivity at $T_c \sim 20$ K and ~ 30 K, respectively. A recent study indicated a possibility of $T_c \sim 150$ K when femtosecond laser pulses excite phonon-modes of K₃C₆₀ under 0.3 GPa⁶. Alternatively, charge-transfer (CT) complex of C₆₀ with electron-donating molecule undergoes paramagnetic-ferromagnetic transition at $T_c \sim 17$ K⁷. Moreover, photoinduced CT processes between fullerene derivatives and π -conjugated polymers efficiently generate electron-and-hole carriers with enhanced mobilities, enabling to improve a performance of organic photovoltaic solar cells^{8,9}.

Alternatively, early photoluminescence (PL) studies have already elucidated that i) fullerenes can emit fluorescence (FL), but in very low quantum yields (QEs)¹⁰⁻¹³, ii) the singlet (S₁)-triplet (T₁) intersystem crossing (ISC) occurs nearly quantitatively due to large spin-orbit (SO) coupling¹⁴, and hence, iii) a thermally activated delayed FL (TADF) is possible due to a small S₁-T₁ energy gap (ΔE_{S-T})¹⁵⁻¹⁹. The lack of a high QE fluorescence at S₁-S₀ transition, hence, remains obstacle when fullerene derivatives are applied to several photonic applications.

Molecular chirality and helicity play the key role in biomolecular and human-made materials science, facilitating an introduction of a perturbation to the photoexcited and ground states. Most chiral organic luminophores in solutions reveal circularly polarized luminescence (CPL) in UV-visible region²⁰. A few helicenes as helical nanocarbon molecules emit CPL in the visible region up to 800 nm^{21,22}. To overcome those drawbacks of fullerenes, we rationally designed π -surface of C₇₀ to modulate chiral

electronic structures²³⁻²⁵. To this end, the enantiomerically pure C₇₀ derivatives, **X70A**, were newly synthesized by reacting bis-borylated xanthene with C₇₀ in a one-step double addition reaction, followed by a successful purification using a careful HPLC technique with chiral separation column.

Here, we showcased the first deep-red color mirror-image CPL spectra at 690 nm from the fullerene derivative associated with the corresponding mirror-image circular dichroism (CD) spectra when left-handed and right-handed **X70A** are dissolved in toluene. The CPL-function **X70A** should apply to invisible security gates in deep-red to near infrared (NIR) region in future²⁶.

Results

Molecular and reaction designs. Because C₇₀ has five nonequivalent carbons (*a-e*, in Fig. 1a), specific *a* and *b* atoms with a high angular distortion closer to two poles have inherently a high reactivity toward several nucleophiles²⁷. The reactivity of α site (*a-b* double bond) and β site (*c-c* double bond) is higher than other sites, facilitating to rationally design the double bond selective reaction²⁸⁻³¹. When two C-C double bonds are inequivalent to a symmetrical plane, C₆₀ and C₇₀ become chiral electronic structures due to symmetry breaking. In 1998, Diederich et al. synthesized originally racemic mixtures of bis-adducts of C₆₀ and C₇₀ by the Bingel reaction³², leading to a successful resolution of enantiomerically pure compounds.

After a nucleophilic reaction of a substrate on the most reactive carbon α of C₇₀, when the second addition reaction can be performed regioselectively on the successive β site (*c-c* double bond), the resulting bis-adduct will be chiral (Fig. 1b). This tether-directed remote functionalization³³⁻³⁵ was first achieved for the selective preparation of C₆₀ tris- adduct³³. This time, we reacted two boronic acids with a fixed short distance on C₇₀ with a rhodium catalyst using Itami's method^{36,37}. Xanthene skeleton was chosen as very short- tethered boronic acids. Bis-borylated xanthene **1** was prepared from 4,5-dibromo-2,7-di- tert-butyl-9,9-dimethylxanthene in 72% yield³⁸.

Isolation and characterization of X70 family. Bis-borylated xanthene **1** was reacted with C₇₀ in the presence of a catalytic amount of [Rh(cod)(MeCN)₂]BF₄ in H₂O/*o*- dichlorobenzene (1/4) at 60 °C for 6 hrs, followed by the production of the desired xanthene adducts (Fig. 1c)³⁶. The Buckyprep chromatogram (toluene/hexane = 1:1, v/v) of the reaction mixture is given in Supplementary Figure 1. By analysing mass spectrometry of the products, the first eluent is bis-xanthene adducts, and six mono-xanthene adducts are simultaneously formed. The six mono-xanthene adducts are named **X70A**, **X70B**, **X70C**, **X70D**, **X70E**, and **X70F**. The total yield of **X70A** is moderately high of ~ 20%.

¹H NMR spectra of **X70A**, **X70B**, **X70C**, **X70D** are shown in Figure 2. Red and blue circles are assigned to the proton peaks of xanthene and fullerene, respectively. Asymmetric **X70A** was characterized as four doublet peaks due to xanthene and two singlet peaks from the fullerene framework. The two singlet peaks of the fullerene framework taught that C₇₀ carbons at the 1,3-positions (mostly carbons *a* and *c*)

have preferentially reacted. A highly symmetric **X70B** is suggested by two doublet peaks of xanthene and one singlet peak of the fullerene framework, indicating that equivalent carbons *b* had reacted. Two doublet peaks of the fullerene framework in **X70C** indicate the fact that nonequivalent carbons at the 1,4-positions of C₇₀ were reacted. **X70D** shows one singlet peak of fullerene and five peaks of xanthene, suggesting that only carbon *a* was reacted.

The structures of **X70A** and **X70B** were determined by single crystal X-ray structure analysis (Fig. 3d and 3e). **X70A** is a product of double additions at the 1,3-positions of the top six-membered ring of C₇₀, resulting in the generation of the chiral structure. Alternatively, **X70B** was added to carbons *b* at the 1,4-positions of C₇₀, supported from ¹H NMR spectrum.

High-resolution matrix-assisted-laser-desorption/ionization time-of-flight mass spectrometry (HR-MALDI-TOF-MS) of **X70E** and **X70F** detected **X70A** plus 32 mass units, suggesting that the two oxygen atoms are inserted into the mono-xanthene adduct. The ¹H NMR spectral pattern of **X70F** in CDCl₃ is similar to that of **X70A**, exhibiting four doublet peaks due to xanthene and two singlet peaks at 6.44 and 4.86 ppm (Supplementary Fig. 8).

The structure of **X70F** is unambiguously determined by X-ray diffraction analysis, showing that one of the C-C bonds was cleaved by oxygen (Fig. 3f). The product has one hydroxy group on xanthene and one oxygen atom on β-site, indicating an epoxide structure. We are aware of the fact that the singlet peak at 6.44 ppm disappeared after the addition of methanol-*d*₄. Although the formation mechanism of **X70F** remains obscure, **X70F** was gradually generated from **X70A** in solution under air. Similarly, **X70E** is an oxidized form of **X70B** from ¹H NMR analysis (Supplementary Fig. 7).

Photophysical properties of Enantiomerically Pure X70A and X70F. The UV-visible absorption spectra of **X70A**, **X70F**, and pristine C₇₀ are shown in Figure 4a. From the UV-visible spectra of **X70A** and **X70F**, the characteristic peaks of C₇₀ were greatly suppressed and broadened.

Next, we employed an enantiomer resolution from racemates of **X70A** and **X70F** using chiral separation column chromatography. Although a chromatogram of **X70A** in hexane/*i*PrOH (4:1) did not show well-separated peaks after 24-recyclings of the racemate, the first and second half of the peaks clearly provided mirror-signed CD spectral profiles, indicating that the enantiomer resolution is possible (Supplementary Fig. 18). A further four-time repetitions of the enantiomer resolution process using the first half of the peak succeeded in isolation of enantiomerically pure chiral **X70A**_{39,40}. Another enantiomerically pure chiral **X70A** was afforded by using the second half of the peak of **X70A** in the same way (Supplementary Fig. 19). Enantiomerically pure **X70Fs** were obtained from the same separation procedure (Supplementary Figs. 20 and 21). As a result, **X70A1** and **X70A2** as the first and second fractions, respectively, revealed the ideal mirror-image CD spectra ranging from 300 nm and 700 nm (Fig. 4b). The first and second fractions of **X70F** are named **X70F1** and **X70F2**, respectively, in this work (Fig. 4c).

The FL spectra of **X70A** and **X70F**, and for comparison, C_{70} excited at 500 nm in degassed toluene at 20 °C are depicted in Fig. 5a. **X70A** and **X70F** have similar broad FL bands with vibronic shoulders ranging from 600 nm and 850 nm; the FL peak intensities at 670 nm and 680 nm of **X70A** and **X70F** are high by two times and four times, compared to that of C_{70} at 660 nm, respectively (Supplementary Fig. 17). Although the FL emission around 700 nm cannot be recognized by tricolor rhodopsin of human-being eyes owing to out-of-range in sensing, photosensitivity using a crystal silicon-based digital camera can detect up to 950 nm, allowing us to clearly capture the deep-red emission (inset of Fig. 5a). The FL lifetimes of **X70A** and **X70F** in the deaerated toluene (3.0×10^{-5} M) are 0.99 ns and 1.31 ns, respectively.

The enantiopure **X70A1** and **X70A2** clearly displayed mirror-image CPL spectra (Fig. 5b). To the best of our knowledge, these CPL spectra are the first fullerene-based CPL although optically active C_{76} , C_{82} , C_{84} and C_{60}/C_{70} with adducts were isolated and FL among these was reported in the 1990s. The absolute *glum* values of **X70A1** and **X70A2**, $|glum|$, was moderately high: 7.0×10^{-3} ($\lambda_{ex} = 600$ nm, $\lambda_{em} = 690$ nm). The *glum* value is one of the highest values in deep-red and NIR regions among purely organic compounds in the absence of lanthanide metals⁴¹. Curiously, any obvious CPL signals of **X70F1** and **X70F2** were not observed (Fig. 5c). To provide a possible explanation, we calculated the intersection of the electric and magnetic transition dipole moments of **X70A** and **X70F**. Interestingly, although **X70F** has two orthogonal electric and magnetic dipole moments, **X70A** is not (Supplementary Fig. 27). The orthogonal electric and magnetic dipole moments should result in the cancelation of the $|glum|$ values, leading to the fact that CPL was largely diminished⁴².

Discussion

Until now, the photochemistry of fullerenes has mainly focused on subsequent electron transfer after photoexcitation and triplet energy transfer, for example, through the generation of singlet oxygen. The present outcome clearly demonstrates the potent application when fullerene-based PL (and FL) are used as photonic device materials. We successfully synthesized and characterized a family of xanthene-attached C_{70} derivatives **X70n** by a facile one-step reaction from C_{70} . Furthermore, we succeeded in enantiomer separation from racemates of **X70A** and **X70F**. It was found that **X70A** and **X70F** emit stronger by two and four times relative to C_{70} , respectively. The enantiomeric pair of **X70A** clearly revealed the ideal mirror-image CPL spectra ranging from deep-red to NIR regions with a considerably large $|glum|$ value of 7×10^{-3} at 690 nm as a purely organic fluorophore. We believe that the pure enantiomers and racemates of chiral fullerene derivatives should exhibit a long-lived TADF originated from the small ΔE_{S-T} ,⁴³ affording significantly advantages toward purely organic luminophores in realizing NIR photonic devices⁴⁴.

Methods

General methods. C_{70} (purchased from SES research Inc.) was purified by Buckyprep column and degassed at room temperature before spectroscopic measurements. See Supplementary Methods for

further details.

Synthesis of X70A to X70F. A Schlenk flask was flame-dried under vacuum and filled with argon. To this flask were added dry *o*-dichlorobenzene (140 mL) and H₂O (36 mL) under a stream of argon. After performing three freeze-pump-thaw cycles, [Rh(cod)(MeCN)₂]BF₄ (45 mg, 0.18 mmol), C₇₀ (500 mg, 0.59 mmol), and 2,7-di-*tert*-butyl-9,9-dimethylxanthene-4,5-diboronic acid (275 mg, 0.71 mmol) were added to the flask under a stream of argon. After stirring the mixture at 60 °C for 6 h, the mixture was cooled to room temperature. The organic layer was separated and passed through a pad of Celite and silica gel, washing with toluene. The filtrate was concentrated and purified by Buckyprep column (toluene/hexane (v/v) = 1:1 eluent) to afford **X70A** (140 mg, 20%), **X70B** (0.8 mg, 0.1%), **X70C** (12 mg, 1.0%), **X70D** (13 mg, 1.1%), **X70E** (0.7 mg, 0.1%) and **X70F** (3.1 mg, 0.3%) as brown solids. **X70A**: ¹H NMR (500 MHz, CDCl₃): δ = 8.03 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H), 7.28 (d, *J* = 1.5 Hz, 1H), 6.76 (d, *J* = 2.0 Hz, 1H), 5.17 (s, 1H), 3.17 (s, 1H), 1.91 (s, 3H), 1.89 (s, 3H), 1.52 (s, 9H) and 1.20 (s, 9H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 159.48, 155.70, 154.92, 152.98, 152.71, 152.68, 152.34, 152.00, 151.15, 151.13, 150.34, 149.93, 149.89, 149.78, 149.65, 149.02, 148.97, 148.70, 148.64, 148.26, 148.17, 147.99, 147.62, 147.31, 147.29, 147.12, 147.09, 147.01, 146.98, 146.86, 146.76, 146.65, 146.41, 146.33, 146.10, 145.98, 145.82, 145.69, 145.64, 145.44, 145.36, 145.29, 145.05, 144.95, 144.92, 144.54, 144.21, 144.17, 144.04, 143.53, 143.36, 143.06, 142.79, 141.99, 141.86, 140.15, 139.90, 139.71, 139.24, 135.71, 135.50, 133.88, 133.79, 132.85, 132.79, 132.59, 132.23, 132.23, 131.46, 131.10, 128.90, 121.29, 120.63, 119.79, 118.94, 68.01, 63.19, 58.15, 50.41, 41.02, 35.63, 35.24, 32.22, 31.89, 29.02 and 22.70 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for C₉₃H₃₀O, 1162.2291 [*M*]⁺; found: 1162.2288; UV-vis (toluene): λ_{max} (ε[10³ M⁻¹cm⁻¹]) = 360 (20.3), 401 (22.1), 533 (7.15), 579 (4.93) and 632 (2.92) nm. **X70B**: ¹H NMR (500 MHz, CDCl₃): δ = 7.68 (d, *J* = 2.0 Hz, 2H), 7.29 (d, *J* = 1.5 Hz, 2H), 5.26 (s, 2H), 1.79 (s, 3H), 1.64 (s, 3H) and 1.28 (s, 18H) ppm; ¹³C NMR: N.D.; *m/z*: calcd for C₉₃H₃₀O, 1162.2291 [*M*]⁺; found: 1162.2304; UV-vis (toluene): λ_{max} (relative intensity) = 345 (1.00), 375 (0.85), 395 (0.83), 436 (0.94), 472 (0.76), 540 (0.46), 637 (0.12) and 688 (0.10) nm. **X70C**: ¹H NMR (500 MHz, CDCl₃): δ = 8.14 (d, *J* = 1.5 Hz, 1H), 7.50 (d, *J* = 1.5 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 5.61 (d, *J* = 7.0 Hz, 1H), 5.31 (d, *J* = 7.0 Hz, 1H), 1.94 (s, 3H), 1.69 (s, 3H), 1.53 (s, 9H) and 1.27 (s, 9H) ppm; ¹³C NMR: N.D.; HR-MS (Spiral MALDI): *m/z*: calcd for C₉₃H₃₀O, 1162.2291 [*M*]⁺; found: 1162.2292. **X70D**: ¹H NMR (500 MHz, CD₂Cl₂): δ = 8.18 (d, *J* = 2.5 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.83 (s, 1H), 1.81 (s, 6H), 1.34 (s, 9H), and 1.26 (s, 9H) ppm; ¹³C NMR: N.D.; HR-MS (Spiral MALDI): *m/z*: calcd for C₉₃H₃₀O, 1162.2291 [*M*]⁺; found: 1162.2308; UV-vis (toluene): λ_{max} (relative intensity) = 341 (1.00), 398 (0.86), 468 (0.61), 536 (0.33) and 662 (0.06) nm. **X70E**: ¹H NMR (500 MHz, CD₂Cl₂): δ = 8.27 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 4.95 (s, 1H), 4.81 (s, 1H), 1.98 (s, 3H), 1.58 (s, 3H), 1.57 (s, 9H), and 1.32 (s, 9H) ppm; ¹³C NMR: N.D.; HR-MS (Spiral MALDI): *m/z*: calcd for C₉₃H₃₀O₃Na, 1217.2087 [*M*]⁺; found: 1217.2073; UV-vis (toluene): λ_{max} (relative intensity) = 358 (1.00), 398 (0.87), 588 (0.18) and 657 (0.07) nm. **X70F**: ¹H NMR (500 MHz, CDCl₃): δ = 7.90 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.44 (s, 1H), 4.86 (s, 1H), 1.83 (s, 6H), 1.49 (s, 9H),

and 1.34 (s, 9H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ = 169.03, 168.87, 155.25, 152.36, 152.14, 151.72, 151.33, 151.15, 150.96, 150.77, 150.67, 150.45, 150.14, 150.01, 149.71, 149.68, 149.57, 149.23, 149.13, 149.01, 148.82, 148.65, 148.55, 148.27, 148.09, 148.06, 147.97, 147.73, 147.58, 147.55, 147.51, 147.28, 147.01, 146.68, 146.66, 146.43, 146.41, 146.33, 146.01, 145.88, 145.85, 145.82, 145.65, 145.18, 145.13, 144.73, 144.18, 144.13, 144.06, 144.04, 144.01, 143.88, 143.73, 143.67, 143.64, 143.56, 142.03, 141.33, 139.17, 138.13, 137.79, 134.16, 136.17, 135.84, 135.14, 134.20, 133.99, 133.49, 133.03, 132.53, 132.38, 132.21, 131.76, 131.60, 131.53, 131.44, 131.40, 130.07, 126.36, 124.11, 113.98, 111.51, 81.16, 70.79, 67.25, 59.58, 49.01, 48.98, 35.13, 34.75, 33.39, 33.10, 32.09, 31.79, 31.65, 31.58 and 29.86; HR-MS (Spiral MALDI): m/z : calcd for $\text{C}_{93}\text{H}_{30}\text{O}_3\text{Na}$, 1217.2087 [$M+\text{Na}$] $^+$; found: 1217.2089; UV-vis (toluene): λ_{max} (ϵ [$10^3 \text{ M}^{-1}\text{cm}^{-1}$]) = 399 (20.0), 455 (15.9) and 623 (2.32) nm.

HPLC purification and CD measurement. Preparative HPLC was performed using a ϕ 10 x 250 mm Buckyprep (Nacalai Tesque, Kyoto, Japan) equipped with a JASCO SPD-M10A. Eluent: toluene/hexane = 1/1, v/v. Temperature: at 20 °C. Flow rate: 4.5 mL/min. Injection volume: 5.0 μL . Detection: UV absorption at 326 nm. Chiral resolutions of **X70A** and **X70F** were performed at 20 °C using a ϕ 10 x 250 mm Cholest (Nacalai Tesque) on recycling preparative HPLC with a photodiode array detector SPD-M10A. Eluent: hexane/*i*-PrOH = 4/1, v/v. Flow rate: 4.5 mL/min. Injection volume: 5.0 μL . Detection: UV absorption at 326 nm. CD spectra were recorded using a JASCO J-820 spectropolarimeter.

CPL measurement and analysis. Artefact-free PL and CPL spectra were obtained

using a JASCO CPL-200 spectrofluoropolarimeter, allowing us to avoid second- and third-order stray light due to diffraction grating. The spectrofluoropolarimeter was designed as a prism-based spectrometer with a forward scattering angle of 0° equipped with focusing and collecting lenses, and a movable cuvette holder onto an optical rail enables to adjust the best focal point to maximize PL and CPL signals. A simultaneous CPL and PL measurements allowed to quantitatively evaluate the degree of CPL efficiency relative to PL, known as Kuhn's dissymmetry factor (g_{lum}), that is defined as $g_{\text{lum}} = (I_{\text{L}} - I_{\text{R}})/[(I_{\text{L}} + I_{\text{R}})/2]$, where I_{L} and I_{R} refer to the intensity of left- and right-handed CPL, respectively. The g_{lum} value was practically evaluated as $g_{\text{lum}} = [\text{ellipticity (in mdeg)}/32980/\ln 10] / \text{PL amplitude (in Volts)}$ at the CPL extremum.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information file. For full characterization data of new compounds and experimental details, see Supplementary Methods and Figures in Supplementary Information file. The X-ray crystallographic coordinates for structures **X70A**, **X70B** and **X70F** reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 2013940-2013942. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. All other data are available from the authors upon reasonable request.

Declarations

Acknowledgments

This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Nos. JP20H02816 (H.H.), JP19H04584, JP19K22112, JP20H02711 (N.A.) and JP20H00379 (H.Y.) and CREST JST (no. JPMJCR15F1) (H.Y.). We thank Yoshiko Nishikawa and Yasuo Okajima (NAIST) for MS and FL lifetime measurements, respectively.

Author contributions

H.K. performed the synthetic experiments and collected the central data. M.F. conducted the CPL measurements. N.A. determined the crystal structures. H.K. and K.M. carried out detailed DFT and TD-DFT calculations. N.A. and H.Y. designed and directed the project. H.H., K.M. H.Y. and N.A conducted the methodology and validation. N.A. wrote the manuscript, and all authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

The schematic representation of the short distance tether-directed remote functionalization of C₇₀. (a) Ball-and-stick model of C₇₀ with carbon labels: a (red), b (orange), c (yellow), d (green), and e (purple). (b) The sequential reaction of the tethered-substrate with C₇₀, which is bound to carbon a in the first addition reaction. Here, the second addition reaction is limited to the β site. This is a chiral reaction, depending on whether it is on the left or right, and (c) Reaction of C₇₀ with a bis-borylated xanthene 1 to afford X70n.

Figure 2

^1H NMR spectra of a series of X70n and illustration of the replacement positions on C₇₀. (a) X70A in CDCl_3 , (b) X70B in CDCl_3 , (c) X70C in CDCl_3 and (d) X70D in CD_2Cl_2 . * indicates impurity peaks. Red circles are assigned to the peaks of xanthene and blue ones are assigned to the peaks of fullerene protons. Ca, Cb and Cc in the illustration of fullerene represent the carbons of xanthene bound; Ha, Hb and Hc are the hydrogens attached to carbons a, b and c, respectively. The structures of X70A and X70B determined by the single crystal X-ray analysis are shown in Figure 3. The structures of X70C and X70D suggested from the ^1H NMR spectra are shown in Supplementary Figures 4 and 5.

Figure 3

Structures of X70A, X70B and X70F. Molecular structures of (a) X70A, (b) X70B and (c) X70F and their ORTEP diagrams of single crystal X-ray structures of (d) X70A, (e) X70B and (f) X70F with 25% thermal ellipsoids. Solvent molecules and disordered parts are omitted for clarity.

Figure 4

UV-visible absorption and CD spectra. (a) UV-vis absorption spectra of X70A (blue line), X70F (red line), and for comparison, C70 (black line) in toluene. (b) Blue and red lines represent CD spectra in toluene of the first (X70A1: $9.6 \times 10^{-6} \text{ M}$) and second (X70A2: $5.1 \times 10^{-6} \text{ M}$) fractions, respectively. (c) Blue and red lines represent CD spectra in toluene of the first (X70F1: $6.1 \times 10^{-6} \text{ M}$) and second (X70F2: $5.1 \times 10^{-6} \text{ M}$) fractions, respectively.

Figure 5

FL and CPL/PL spectra of X70A and X70F in toluene. (a) FL spectra of X70A (blue line), X70F (red line), and C70 (black line) in toluene excited at 500 nm with the absorbance adjusted at 0.1. Inset: Photograph of deep-red color FL from X70A1 excited at 450 nm taken by a digital camera (Leica, ASA 6400, f1.8, SS1/4). (b) CPL (top) and PL (bottom) spectra of X70A in toluene excited at 500 nm. Blue and red lines represent CPL/PL spectra of the first and second fractions, respectively. (c) CPL (top) and PL (bottom) spectra of X70F in toluene excited at 500 nm. Blue and red lines represent CPL/PL spectra of the first and second fractions, respectively. Note that X70F showed no obvious CPL spectra.

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