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Planarity of terphenyl rings possessing o-carborane cages: turning on intramolecular-charge-transfer-based emission†

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To clarify the relationship between planarity and intramolecular charge transfer (ICT), two o-carboranyl compounds (TCB and FCB) containing different *ortho*-type terphenyl rings, namely, perfectly distorted or planar phenyl rings, were synthesised and fully characterised. Although the emission spectra of both compounds presented intriguing dual-emission patterns in solution at 298 or 77 K and in the film state, distorted TCB mostly showed locally excited emission, whereas planar FCB demonstrated intense emission corresponding to an ICT transition. Interestingly, the emission efficiencies and radiative decay constants of terphenyl-based *o*-carboranyl compounds were gradually enhanced by increasing the planarity of the terphenyl groups. These results verify the existence of a strong relationship between the planarity of appended aryl groups and ICT-based radiative decay in *o*-carborane-substituted compounds.

The development of novel organic luminophores has led to considerable research into efficient functional materials for prominent optoelectronic applications. For instance, compounds consisting of *o*-carborane (*closo*-1,2-C₂B₁₀H₁₂) linked to organic fluorophores have been widely researched as unprecedented optoelectronic materials^{1–23} for a variety of photonic applications, such as organic light-emitting diodes⁵ and organic field-effect transistors.²¹ These thermally and electrochemically stable compounds exhibit specific photophysical properties resulting from the intrinsic nature of the *o*-carborane unit.^{3,8,13–15} In particular, the strong electron-withdrawing properties^{24–26} of the C atoms in the *o*-carborane cage lead to the formation of electron donor–acceptor dyad systems that induce distinct intramolecular-charge-transfer (ICT) transitions with π -conjugated aromatic substituents,^{27–31} resulting in unique luminescent behaviors. Recently, manipulation of the ICT process

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in o-carboranyl derivatives by strategically designing the molecular geometry has been extensively investigated.^{21,32-40} The C-diazaborylo-carborane-based donor-acceptor dyad system reported by the Fox group demonstrated that diazaboryl-group rotation prevents the emissive ICT mechanism, resulting in the formation of only locally excited (LE) high-energy states.³² Furthermore, a variety of *o*-carboranyl-bearing fluorescent π -aromatic units, such as naphthyl,³³ anthracenyl,³⁴⁻³⁶ tetraphenylethenyl,³⁷ pyrenyl,³⁸ chrysenyl,³⁹ and benzodithiophene,⁴⁰ display multiple photoluminescence (PL) bands originating from twisted intramolecular charge-transfer (TICT) states. Such features were also observed for structural variations of the aryl group linked to the o-carborane cage. By comparing the photophysical properties of o-carboranyl biphenyl and fluorene compounds, our group found that the emissive ICT transitions showed a dramatic dependence on the planarity of the biphenyl rings.²¹ These results suggested that the emissive characteristics of o-carboranyl compounds are controlled by the structural arrangement the aryl moieties and o-carborane cage as well as by the structural features of the appended aromatic groups themselves. Although studies on various aryl groups appended to o-carborane cages and their ICT behaviors have clearly revealed that geometrical arrangements between aryl moieties and o-carborane play important roles in controlling the intrinsic electronic characteristics, the influence of structurally varying the appended aromatic groups themselves on the photophysical properties has rarely been investigated in detail.

Thus, to explore the dependence of the intramolecular electronic characteristics on structural features, in particular the planarity, and to gain in-depth insight into this relationship, *o*-carboranes were coupled with 2',5'-dimethyl-1,1':4',1''-terphenyl (perfectly distorted *o*-terphenyl rings) and 6,6,12,12-tetramethyl-6,12-dihydroindeno[1,2-b]fluorene (perfectly planar *o*-terphenyl rings). We report herein the synthesis and photophysical properties of two terphenyl-based *o*-carboranyl compounds (Fig. 1a, **TCB** and **FCB**) and compare their radiative decay efficiencies for ICT-based emission with those of reported terphenyl-based (compound 2^{41}) and fluorene-based ($2\mathbf{F}^{21}$) *o*-carboranyl compounds. These strategic,

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Fig. 1 (a) Synthetic routes for the terphenyl based *o*-carboranyl compounds **TCB** and **FCB**. Reaction conditions: (i) 1-hexyne, Cul, Pd(PPh₃)₂Cl₂, triethylamine/toluene, r.t., 24 h. (ii) $B_{10}H_{14}$, diethyl sulfide, toluene, 110 °C, 72 h. (b) X-ray crystal structure of **TCB** (50% thermal ellipsoids with H atoms omitted for clarity).

systematic studies revealed that the radiative decay efficiency of ICT-based emission is significantly affected by the planarity of appended aromatic groups.

The synthetic routes for the terphenyl-based o-carboranyl compounds (TCB and FCB) are shown in Fig. 1a. Detailed synthetic procedures for the dibromo precursors (TBr and **FBr**) can be found in the Experimental section in the ESI.[†] Sonogashira coupling between 1-hexyne and TBr or FBr produced the acetylene-substituted compound, TAC or FAC, in moderate yield (40% for TAC and 50% for FAC). Finally, the o-carborane-appended ortho-type-terphenyl compound, TCB or FCB, was prepared from TAC and FAC using a decaborane (B10H14)-promoted cage-forming reaction in the presence of a weak base.^{42–44} The terminal *n*-butyl groups of both the *o*-carboranyl cages and dimethyl groups in FCB were introduced to achieve good solubility in various organic solvents. All precursors and o-carboranyl compounds were fully characterised by multinuclear NMR spectroscopy (Fig. S1-S14, ESI⁺) and elemental analysis. In particular, two broad singlet peaks between -3 and -13 ppm in the ¹H-decoupled ¹¹B NMR spectra of **TCB** and **FCB** clearly confirm the presence of the closo-carborane cage in each compound. In addition, TCB was subjected to X-ray crystallography, and the elucidated solid-state molecular structure is displayed in Fig. 1b. The structure clearly reveals a central terphenyl group with appended o-carborane cages.

To investigate the photophysical properties of the terphenylbased *o*-carboranyl compounds **TCB** and **FCB**, UV-vis absorption and PL measurements (Fig. 2 and Table 1) were performed. **TCB** and **FCB** exhibited a dominant low-energy absorption



Fig. 2 UV-vis absorption and PL spectra for (a) **TCB** (λ_{ex} = 298 nm) and (b) **FCB** (λ_{ex} = 351 nm). Inset figures show the emission colour in each state under irradiation by a hand-held UV lamp (λ_{ex} = 295 nm for **TCB** and 365 nm for **FCB**).

band at $\lambda_{abs} = \sim 272$ and 356 nm, respectively, in THF, which is associated with the major spin-allowed π - π * LE transition of the center phenylene group, as well as typical ICT transitions between the o-carboranyl cage and the central phenyl rings (see the electronic transition results from time-dependent density functional theory (TD-DFT) calculations below). The emissive properties of both compounds were further examined by PL spectroscopy under a variety of conditions (Fig. 2 and Table 1). Although the PL spectra of TCB and FCB in THF both exhibited dual-emission patterns when excited at 298 and 351 nm, respectively, the emission of TCB was focused in the high-energy region centered at $\lambda_{\rm em} = \sim 350$ nm, whereas FCB exhibited intense low-energy emission in the range of 450-600 nm, which tailed off at 650 nm. With reference to the results of our computational study (vide infra), the high-energy emission originates from $\pi - \pi^*$ transitions of the central terphenyl group, corresponding to LE emission. In contrast, the low-energy emission is closely associated with ICT transitions between o-carborane cages and the terphenyl moiety. The high-energy emission of TCB was relatively unchanged in various solvents with different polarities, whereas the low-energy emission of FCB was dramatically altered (Table 1 and Fig. S16, ESI[†]), showing a solvatochromic effect. These results also strongly indicate that TCB and FCB have LE- and ICT-based emissive characteristics, respectively. Thus, it is evident that the planarity of the terphenyl rings plays an important role in controlling the intramolecular electronic transitions as well as the corresponding radiative decay mechanism. Although TCB showed weak trace only for ICT-based emission in solution (THF solution at 298 K), it exhibited a little enhanced ICT-based emission in the rigid states (THF solution at 77 K and films of 5 wt% doped in poly(methyl methacrylate) (PMMA)). This behavior originates from the increased efficiency of the radiative decay associated with the ICT transition in the rigid molecular state, which restricts structural fluctuations such as C-C bond variations in the o-carborane cage.11,12,21,23

To obtain insight into the relationship between the radiative decay mechanism for the ICT-based emission and the terphenyl group planarity, the quantum efficiencies (Φ_{em}) and decay lifetimes (τ_{obs}) of **TCB** and **FCB** in the low-energy region (**TCB**: 400–550 nm, **FCB**: 420–650 nm) were estimated in THF solution and in films at 298 K (Table 1 and Fig. S17, S18, ESI†). An emission decay lifetime of 0.3–6.9 ns was determined for both compounds, indicating that the observed emission corresponds to fluorescence. The Φ_{em} values of **FCB** in THF at 298 K and in the film were 4% and 56%, respectively, whereas those

Table 1 Photophysical data for terphenyl-based o-carboranyl compounds TCB and FCB

), in THE/nm		$\lambda_{\rm em}/{\rm nm}$												
	$\frac{\lambda_{\rm abs} \text{m} \text{I} \text{HF/IIII}}{\left(\varepsilon \times 10^{-3} \text{M}^{-1} \text{cm}^{-1}\right)}$	$\lambda_{\rm ex}/{\rm nm}$	Toluene ^a	THF ^a	DCM ^a	77 K ^b	Film ^c	$\Phi_{\mathrm{em}}{}^d$		$\tau_{\rm obs}/r$	ns	$k_{\rm r}^{\ e}/\times 1$	$0^7 \ {\rm s}^{-1}$	$k_{\rm nr}^{f}/\times 1$	$0^8 s^{-1}$
тсв	272 (47.0)	298	349	350	349, 526	345, 484	348, 495	< 0.01	0.016	g	6.90	_	0.29	_	1.4
FCB	340 (42.0), 356 (49.3)	351	375, 504	375, 548	376, 560	509	514	0.042	0.563	0.28	2.60	15.0	21.7	34.2	1.7
a c = PL q	5.0 $ imes$ 10 ^{-5} M, observed uantum yield. e $k_{ m r}$ = $\Phi_{ m e}$	at 298 K m/ τ_{obs} .	$k_{\rm nr}^{b} c = 5.0 > k_{\rm nr} = k_{\rm r} (1/4)$	$(10^{-5} \mathrm{M~ir})_{\mathrm{em}} = 1$). g	n THF, obs Not meas	erved at 77 ured due f	7 K. ^c Meas to weak en	sured in t nission.	he film	state	(5 wt%	6 dope	l in PMN	MA). ^d A	bsolute

for TCB were much lower (only 2% in the film state). The radiative decay constant (k_r , 2.2 × 10⁸ s⁻¹, Table 1) for ICT-based emission in the FCB film, calculated from the $\Phi_{\rm em}$ and $\tau_{\rm obs}$ values, was more than 70 times larger than that of the TCB film $(0.3 \times 10^7 \text{ s}^{-1})$. In contrast, the nonradiative decay constants for the films of both compounds were similar ($k_{\rm nr}$, 1.4 \times 10⁸ s⁻¹ for TCB and $1.7 \times 10^8 \text{ s}^{-1}$ for FCB, Table 1). Interestingly, as the center phenyl rings become more planar (TCB: fixed distortion of terphenyl rings \rightarrow compound 2:⁴¹ terphenyl rings that can freely rotate $\rightarrow 2F$ ²¹ fluorene group $\rightarrow FCB$: perfectly planar terphenyl rings), the radiative decay constants for ICT-based emission in the film state are gradually enhanced (*i.e.*, $0.3 \times 10^7 \text{ s}^{-1}$ for TCB \rightarrow 0.8 \times 10⁷ s⁻¹ for compound 2⁴¹ \rightarrow 7.8 \times 10⁷ s⁻¹ for $2\mathbf{F}^{21} \rightarrow 2.2 \times 10^8 \text{ s}^{-1}$ for FCB). Furthermore, the $k_{\rm nr}$ values for compound 2^{41} ($\Phi_{\rm em} = 7.8\% \rightarrow k_{\rm nr} = 1.0 \times 10^8 \, {\rm s}^{-1}$) and $2{\rm F}^{21}$ $(\Phi_{\rm em} = 36.8\% \rightarrow k_{\rm nr} = 1.3 \times 10^8 \, {\rm s}^{-1})$ are similar to those for TCB and FCB. These results strongly indicate that maintaining the planarity of the aromatic rings linked to the o-carborane cages can increase the radiative decay based on ICT transitions involving an o-carborane cage.

TD-DFT calculations on the optimised ground (S_0) and first excited state (S_1) structures of **TCB** and **FCB** revealed the origin of their intramolecular electronic transitions (Fig. S19-S21 and Table S3, ESI[†]). The calculated geometries were optimised based on the X-ray crystal structure of TCB. The computational data for the S₀ state show that the lowest-energy electronic transition for both compounds is the HOMO \rightarrow LUMO transition (Fig. S19 and Table S3, ESI[†]). The HOMOs of both compounds are localised on the central terphenyl rings (>95%, Tables S5 and S7, ESI[†]), whereas the orbital contribution of the *o*-carborane moieties to the LUMOs is slightly higher (>24%). These results indicate that the lowest-energy absorption band of both compounds can be mainly attributed to π - π * transitions of the terphenyl moieties, with a minor contribution from ICT transitions between the o-carborane cages and the terphenyl groups. All the calculated data for the optimised S₀ structures show good agreement with the experimental UV-vis absorption spectra. In contrast, based on the computational data for the S1 structures of TCB and FCB, both the HOMO \rightarrow LUMO and LUMO+1 transitions make major contributions to the low-energy emission band (Fig. S19 and Table S3, ESI⁺). While the LUMOs of both compounds show significant localisation on the o-carborane moieties (>80%, Tables S5 and S7, ESI⁺), the HOMOs are mostly localised on the central terphenyl groups (>92%). These results strongly suggest that the experimentally observed emission in the low-energy region predominantly originates from ICT between the o-carborane cage and the aryl rings, resulting in ICT-based emission. In addition, for each compound,

the LUMO+1 is mostly localised on the central terphenyl group (>83%, Tables S5 and S7, ESI†), strongly suggesting that the intense emission in the high-energy region (centered at ~350 nm for **TCB** and ~375 nm for **FCB**) originates from π - π * transitions of the terphenyl rings, namely LE-based emission. These theoretical calculations allowed precise analysis of all the electronic transitions occurring in each *o*-carboranyl compound.

The optimised geometries of **TCB** and compound 2^{41} provide further evidence for the relationship between the ICT-based radiative decay efficiency and the planarity of the terphenyl rings. The optimised S₀ structure of TCB exhibited significantly distorted aryl groups, with the dihedral angles between the center phenyl ring and each side phenyl ring calculated as $\Psi_1 = 50.3^\circ$ and Ψ_2 = 53.2° (Table 2). These values are similar to those in the solid-state molecular structure of TCB (53.8° and 55.9°, Table 2). Interestingly, the dihedral angles in the optimised S₁ structure of **TCB** decreased significantly $(38.0^{\circ} \text{ and } 42.1^{\circ}, \text{ Table 2})$, despite the steric repulsion of the methyl groups on center phenyl ring. This observation indicates that the terphenyl moiety prefers to be planar in the excited states. Distinct structural features are observed in the optimised S_0 and S_1 geometries of compound 2.⁴¹ Compared with **TCB**, the dihedral angles ($\sim 35^{\circ}$, Table 2) in the S₀ structure of compound 2 were much smaller, and these values further decreased to $\sim 22^{\circ}$ in the S₁ structure. These results imply that the terphenyl moiety adopts a structure that is as planar as possible in the excited states. Consequently, the experimental and theoretical features of these terphenyl-based o-carboranyl compounds confirm that the planarity of the terphenyl rings strongly influences the efficiency of the radiative

Table 2 The dihedral angles (Ψ_1 and Ψ_2) between terphenylene rings for TCB and compound ${\bf 2}^{41}$

	$R = CH_3, TCB$ $R = H, Compound 2$										
	тсв			Compound 2							
		Calc. ^b		Calc. ^b							
	Exp. ^a	S ₀	S ₁	So	S ₁						
$\Psi_1/^\circ$	53.8	50.3	38.0	34.5	21.9						
$\Psi_2/^\circ$	55.9	53.2	42.1	36.7	21.8						

 a Experimental values from the X-ray crystal structures. b Calculated values from their ground (S_0) and the first excited singlet state (S_1) optimised structures.

decay for the ICT transition involving the *o*-carborane moiety. Furthermore, these results imply that linking planar aryl rings to *o*-carborane cages can turn on the ICT-based radiative decay mechanism.

In conclusion, we prepared and characterised distorted and planar terphenyl-based *o*-carboranyl compounds (**TCB** and **FCB**). The solid-state structure of **TCB** showed perfectly distorted terphenyl rings. Although **TCB** exhibited LE-based emission in THF at 298 K, under the same conditions, **FCB** demonstrated intense emission that was attributable to ICT transitions involving the *o*-carborane cage. Interestingly, increasing the planarity of the terphenyl group enhanced the quantum efficiency and radiative decay efficiency. Consequently, these results definitively indicate that the planarity of the aryl groups appended on *o*-carborane is critical for controlling the ICT-based radiative decay of *o*-carborane substituted compounds.

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Conflicts of interest

There are no conflicts to declare.

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