■ Luminescent Materials

Tetrakis{[(p-dodecacarboranyl)methyl]stilbenyl}ethylene: A Luminescent Tetraphenylethylene (TPE) Core System

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Abstract: The synthesis and spectroscopic characterization of the first set of tetrakis{[(p-dodecacarboranyl)methyl]-stilbenyl}ethylenes (TDSE), substituted either with a methyl or a phenyl group in the 2-position ($C_{cluster}$) of the ortho-carborane, are described. The complex absorption properties are elucidated by TD-DFT calculations, stressing the importance of through-bond conjugation. Enhanced conjugation and restric-

tion of the conformational space are identified as the main factors for boosted luminescence properties in solution, compared with the tetraphenylethylene (TPE) core, effectively reducing internal conversion (IC). IC is further reduced when aggregate suspensions of our compounds are formed in water, providing highly luminescent materials of quasi-isolated (very weakly interacting) emitters.

Introduction

Carboranes are icosahedral boron clusters with a three-dimensional delocalization of the electrons, which have unique properties, such as highly polarizable σ-aromatic character,[1] high thermal and chemical stability,[2] and special photophysical and electronic properties that make them useful in biomedical applications and materials science.[3] One of the more recent uses of boron clusters in materials science is the preparation of luminescent materials.[3b,4] In the last decade, several groups have been interested in combining organic π-conjugated systems with carborane derivatives, in order to modulate their electronic, optical, and/or photophysical properties.[4a,4b,4j,5] Our group has also contributed, with rather small conjugated ligands, that is, styrenes, fluorenes, anthracenes, or stilbenes,[6] which need to be extended to modulate systems for materials science applications. In the quest of possible conjugated systems, we selected compounds with relevance in organic opto-

electronics. In fact, in the last few years, compounds that show fluorescence enhancement in the solid state have attracted significant interest due to their applications in (bio)sensing and optoelectronics.[7,8] In many cases, simple cooling (i.e., a frozen environment) or solid solutions (e.g., in PMMA) are sufficient to generate this effect, due to the constraints of the solid environment, which effectively reduce nonradiative deactivation.[8] The mechanism of the latter can vary significantly; for instance, in an early example, stilbene fluorescence is greatly enhanced upon cooling, due to the suppression of trans-cis isomerization;[9] a later report discusses stilbenoid compounds with cyano substitution in the vinylene unit, where nonradiative decay through internal conversion (IC) is promoted by slow torsional relaxation.[10]

Similar arguments were made early on for tetraphenylethylene (TPE).[11] Over the years, TPE has been demonstrated to be a versatile building block for the design and construction of highly luminescent functional materials for OLEDs.[12] To the best of our knowledge, however, of all of the TPE-based systems with extended conjugation reported in the literature, only one example was examined where benzene was replaced by stilbene to give tetraphenylethylene-core stilbene compounds (TSE compounds).[13]

In the current work, we have substituted TSE in the terminal carbon atoms for o-carborane fragments through methylene linkers, giving tetrakis{[(p-dodecacarboranyl)methyl]stilbenyl}-ethylenes (TDSE), optionally substituted with either a methyl or a phenyl group in the 2-position ($C_{cluster}$, C_c) of the ortho-carborane (**Me-TDSE**, **Ph-TDSE**). Herein, we describe the synthesis and characterization of these new compounds, focusing on their optical and photophysical properties, conducting quantitative steady-state and time-resolved fluorescence studies. To rationalize the spectral characteristics of TDSE, we use (time-dependent) density functional theory, (TD-)DFT, computing geometries,

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molecular-orbital (MO) energies and topologies, and relevant excited states of **Me-TDSE**.

Results and Discussion

Synthesis and Characterization of Me-TDSE and Ph-TDSE

The synthesis of carboranyl-containing TDSEs (Scheme 1) was performed by Heck coupling reactions between tetrakis-(*p*-bromophenyl)ethylene (TBPE) and the appropriate (carboranylmethyl)styrene derivatives **1** and **2**, which were previously synthesized from $1\text{-Me-}1,2\text{-}C_2B_{10}H_{11}$ and $1\text{-Ph-}1,2\text{-}C_2B_{10}H_{11}$, according to literature procedures.[6f] The Heck reactions were performed overnight in toluene solutions of **1** or **2** with TBPE, using *N,N*-dicyclohexylmethylamine (NCy_2Me) as a base and $[Pd_2(dba)_3]/[Pd(tBu_3P)_2]$ as catalysts, at 80 °C (Scheme 1). After a few hours, the mixtures changed from black to intense-yellow, suggesting the formation of **Me-TDSE** and **Ph-TDSE**, which were isolated by precipitation with CH_3OH from the reaction mixture as bright-yellow solids. Other Heck reactions using TBPE to give stilbenoid derivatives in 45 % and 21 % yield have been reported;[13] however, the conditions used here are more efficient,[6a,6b,14] resulting in 62 % and 76 % yields for **Me-TDSE** and **Ph-TDSE**, respectively. The reactions were monitored by ^{1}H NMR spectroscopy to confirm their completion by changes in the aromatic resonances, compared with the starting TBPE (Figure S2).

Compounds **Me-TDSE** and **Ph-TDSE** were fully characterized by ATR-FTIR spectroscopy and ^{1}H{^{11}B} NMR, ^{13}C{^{1}H} NMR, and ^{11}B NMR spectroscopy, as well as elemental analysis. The IR spectra of both compounds show bands around 3025 cm^{-1}, corresponding to aromatics, along with a strong band around 2575 cm^{-1}, due to ν(B–H), characteristic for *closo*-carboranes. The ^{1}H NMR spectrum of **Me-TDSE** shows aromatic resonances in the range $\delta = 7.73\text{–}7.09$ ppm, whereas for **Ph-TDSE**, these appear at lower frequencies ($\delta = 7.73\text{–}6.80$ ppm), due to the influence of the ring current from the C_c-Ph group.[6f] The alkene proton resonances CH=CH were observed for **Me-TDSE** and **Ph-TDSE** as singlets at $\delta = 7.06$ and 7.01 ppm, respectively, whereas for both compounds, individual resonances at $\delta = 3.47$ and 3.10 ppm were attributed to C_c-CH$_2$ protons (Figure S2). The ^{13}C{^{1}H} NMR spectra show the aromatic and vinylic carbon resonances in the range $\delta = 144\text{–}126$ ppm, and resonances from the C_c atoms at $\delta = 83.71$ and 82.08 ppm for **Ph-TDSE**,

whereas for **Me-TDSE**, only one C_c atom resonance was identified at $\delta = 74.83$ ppm. Additionally, a peak at $\delta = 23.68$ ppm, due to C_c-CH$_3$ for **Me-TDSE**, was also observed. The ^{11}B NMR spectra show similar 2:8 patterns with two doublets, ranging from $\delta = -3.75$ to -10.43 ppm, for both compounds.

Optical and Photophysical Properties

The optical properties of **Me-TDSE** and **Ph-TDSE** were studied by UV/Vis spectroscopy and photoluminescence (PL) spectroscopy in THF solutions and in aggregate suspensions of them formed in water. The UV/Vis absorption spectra in solution (Figure 1) show a complex pattern, started by a pre-band at 409 nm (3.00–3.03 eV, A$_1$ band), and the main absorption band at 340 nm (3.66–3.67 eV; A$_2$), with a ratio of the integrated bands of $f(A_1)/f(A_2) = 0.2$ (Figure S3). According to the TD-DFT results for **Me-TDSE**, A$_1$ is assigned to the excitation from the
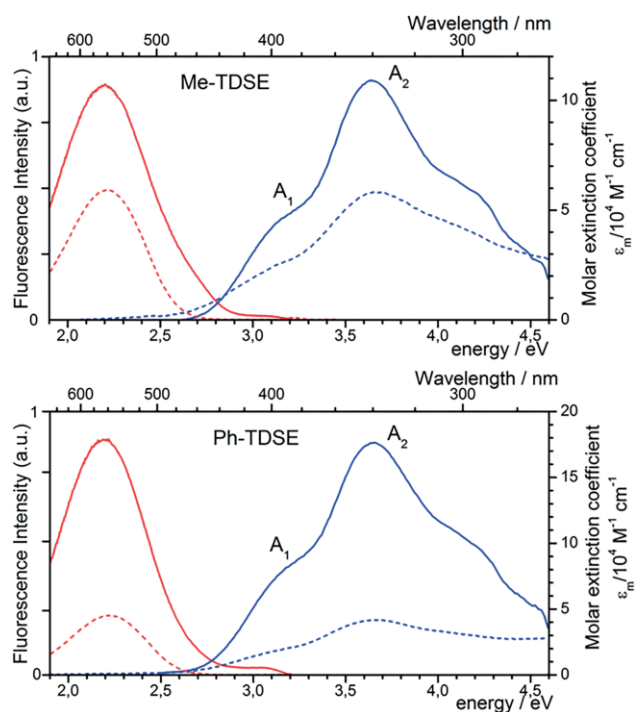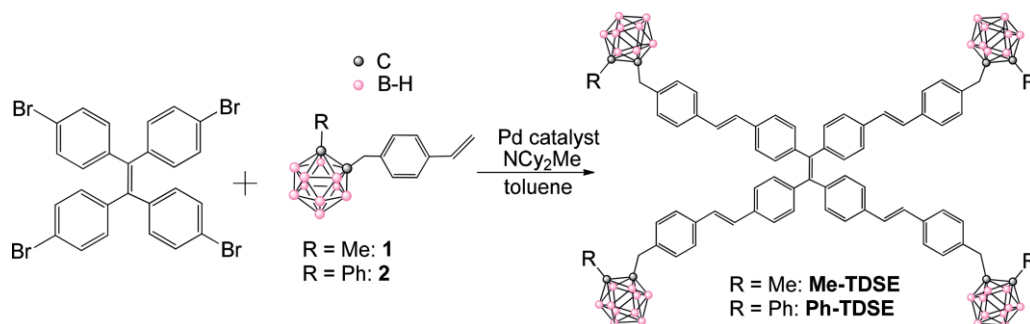

Figure 1. (Right) UV/Vis absorption spectra and (left) fluorescence emission spectra (excitation wavelength 340 nm) of (top) **Me-TDS** and (bottom) **Ph-TDS**, in THF (solid lines) and THF/water (1:1000, v/v; dashed lines).

Scheme 1. Synthesis of **Me-TDSE** and **Ph-PDSE** from **1** and **2**.

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Table 1. Relevant singlet states of **Me-TDSE**, as calculated by TD-DFT: experimental (exp) and calculated (calc) vertical absorption energies E, oscillator strengths f, and their composition with configuration interaction (CI) coefficients and percentages.

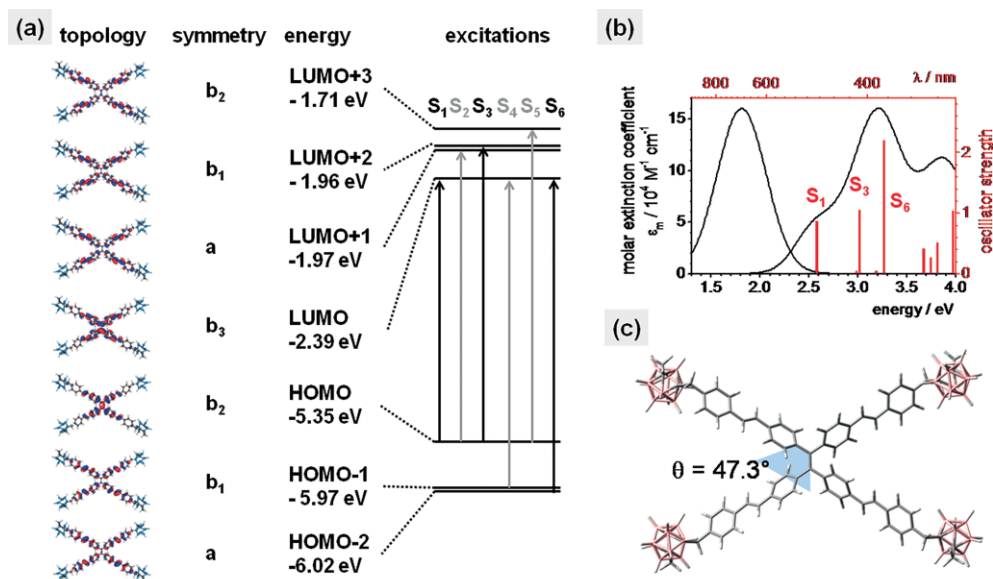| State	E_{exp} [eV] (λ_{max} [nm])	E_{calc} [eV] (f)	Composition
S_1	3.03 (409)	2.58 (0.87)	HOMO→LUMO (0.70; 99 %)
S_2		2.99 (0.05)	HOMO→LUMO+1 (0.70; 99 %)
S_3		3.01 (1.05)	HOMO→LUMO+2 (0.69; 95 %)
S_4		3.18 (0.05)	HOMO−1→LUMO (0.70; 99 %)
S_5		3.26 (0.00)	HOMO→LUMO+3 (0.56; 63 %)
			HOMO−3→LUMO (−0.42; 35 %)
S_6	3.66 (339)	3.26 (2.21)	HOMO−2→LUMO (0.69; 95 %)

Figure 2. TD-DFT calculations of **Me-TDSE**. (a) Topologies, symmetries and energies of relevant MOs in the electronic ground state S_0 and resulting electronic excitations (symmetry-allowed in black, -forbidden in grey). (b) Calculated emission and absorption spectrum (pure electronic transitions, broadened with a Gaussian of 0.25 eV width) with state assignments. (c) Optimized ground-state geometry.

ground to the first excited singlet state (S_0→S_1), with an oscillator strength of $f = 0.87$, described by an excitation from the highest occupied to the lowest unoccupied molecular orbital (HOMO→LUMO); see Table 1 and Figures 2 and S6. Frontier molecular orbitals (FMOs) are significantly spread over the conjugated core (through conjugation),[15] which rationalizes the significant redshift against stilbene. On the other hand, A_2 contains several transitions, with main contributions from S_0→S_2 ($f = 1.05$, HOMO→LUMO+2) and S_0→S_6 ($f = 2.21$, HOMO−2→LUMO); see Table 1. The spectra show no vibronic fine structure, and the effect is significantly stronger than what was reported earlier for stilbene itself;[16] in stilbene, the structureless features mainly arise from the torsional potential around the phenyl–vinyl single bond, which is much more shallow in S_0 than in S_1.[16] In R-**TSDE** (R = Me, Ph), this effect is expected to be significantly enhanced, due to the strongly twisted central TPE unit, as has been calculated for R = Me ($\theta = 47°$, see Figure 2), which leads to a complete loss of vibronic structure.

The fluorescence spectra of both compounds have a peak at $\lambda_{em} = 563$ nm (2.21 eV); they are equally as unstructured as in the absorption spectra, that is, they are very different to that of stilbene, where only the absorption is unstructured (vide supra), but the emission is found to be structured;[16] the unstructured

emission of the TDSE compounds also arises from the twisted TPE unit in the S_1 state (calculated to $\theta = 30°$), due to the steric demands of the molecule; similar effects were, for example, observed for substituted stilbene-type materials.[17]

Me-TDSE and **Ph-TDSE** exhibit fluorescence quantum yields (Φ_F) of 12 % and 15 %, respectively, in THF solution (Table 2). This is noticeably higher than those found for stilbene[18] and the free (carboranylmethyl)stilbene derivatives (7 % and 2.4 %),[6a] and it is consistent with the main nonradiative deactivation pathway in stilbene, that is, through *trans/cis* isomerization,[18] not being followed by the TDSE derivatives. In fact, the nonradiative rates k_{nr} (extracted from τ_F and the intensity-averaged lifetime $<\tau_F>$, see Table 2) are quite short [2.65 ns^{-1} and 2.32 ns^{-1} for Me and Ph substitution, respectively, compared with stilbene (16 ns^{-1})].[18] Comparative studies on substituted TPEs confirm the minor importance of isomerization in TPE-type compounds.[19] Instead, the nonradiative decay in TPE (through IC) invokes large-amplitude torsional relaxation in the first excited state S_1.[11] IC, however, is a complex process; a proper description requires knowledge of the accessible conical intersection between the excited-state potential hypersurface (PHS; i.e., the "energy landscape") and the ground state, rather than simple assumptions about the restriction of intramolecular

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Table 2. Photophysical measurements of **Me-TDSE** and **Ph-TDSE** in solution (THF) and aggregate suspensions (THF/H$_2$O, 1:1000): fluorescence quantum yield Φ_F and lifetimes τ_F (recorded at λ_{exc} = 340 nm), obtained from a bi-exponential fit (fractional intensities f_i are given in parentheses); intensity-averaged lifetime $\langle\tau_F\rangle$; extracted radiative and nonradiative rates by $k_F = \Phi_F/\tau_F$ and $k_{nr} = (1 - \Phi_F)/\tau_F$.

		τ_1, τ_2 [ns]	$\langle\tau_F\rangle$ [ns][a]	λ_{em} [nm]	Φ_F	k_F [ns^{-1}]	k_{nr} [ns^{-1}]
Me-TDSE	THF	1.57 (9 %), 0.21 (91 %)	0.33	563	0.12	0.38	2.65
	THF/water	2.46 (39 %), 0.62 (61 %)	1.34	559	0.51	0.38	0.36
Ph-TDSE	THF	1.15 (14 %), 0.26 (86 %)	0.38	563	0.15	0.39	2.32
	THF/water	1.24 (50 %), 0.85 (50 %)	1.05	561	0.56	0.44	0.35

[a] Intensity-averaged lifetimes were calculated by using $\langle\tau_F\rangle = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2) = f_1 \tau_1 + f_2 \tau_2$, where A_i are the amplitudes and f_i the fractional intensities.[23]

rotational motions (the so-called RIR[11]); this is clearly evidenced by mixed quantum-classical trajectory surface-hopping calculations done on TPE.[20] Consequently, while dissolved TPE itself exhibits a quantum yield of only Φ_F < 1 %, rigid and/or frozen environments (i.e., "solid solutions")[12,21] or ring substitution,[19] which restricts the conformational space, may cause an enhancement of the Φ_F values. Previous studies have shown Φ_F = 0.24 % for TPE in acetonitrile solution, which greatly increases to 49 % in fabricated amorphous film.[21c]

This restriction of the conformational space might also be one factor in the parent TDSE compounds in fluid solutions, due to the size of the carborane substituents. On the other hand, Φ_F is also high in the carborane-free TSE compound.[13] This points to significant changes in the excited-state PHS, compared with TPE, by enhanced conjugation through the stilbene units; this reduces the access to the conical intersection and, thus, minimizes IC. Large-amplitude motions in S$_1$ of TDSE are also involved in the path from the initially generated Franck–Condon region in S$_1$ towards the point of the PHS at which emission takes place; this gives rise to the observed non-exponential fluorescence decay (Table 2), as reported earlier for related compounds.[22]

The absorption and PL properties of **Me-TDSE** and **Ph-TDSE** were also investigated in a solvent mixture of THF/water (1:1000), similar to previous studies performed for TPE derivatives[21c,24] and other fluorophores bearing boron clusters,[5h] where the compounds form an aggregate suspension (see Figure 1 and Table 2). In contrast to (spin-coated) films, the former allows for appropriate recording of the absorption spectrum, due to the low optical density (i.e., avoiding saturation effects),[25] and for easy determination of Φ_F against a known standard. The absorption spectra and emission spectra of compounds in suspensions of THF/water (1:1000) are very similar to those in solution, with emission maxima at around 560 nm (Figure 1). This indicates that only small intermolecular (excitonic) interactions take place; in fact, such exciton effects (so-called H- or J-aggregate formation) can considerably alter the spectral positions, as reviewed earlier.[8] The lack of excitonic interactions is perfectly in line with the strong space-filling properties of the parent TDSE compounds, which do not allow for close contact of the π-conjugated cores, so that the molecules behave rather like isolated entities, in terms of intermolecular interactions. Remarkably, the fluorescence quantum yields of the suspensions increase to 51 % and 56 % for **Me-TDSE** and **Ph-TDSE**, respectively (Table 2), compared with the Φ_F values in solution (12 % and 15 %, respectively). This is

ascribed to an intramolecular effect, that is, a further considerable reduction of IC through the restriction of large-amplitude motions by the solid environment within the aggregate suspensions, as described earlier for related compounds.[10,21c]

Conclusion

Two carborane-containing stilbenoids have been successfully synthesized by Heck coupling reactions between tetrakis(p-bromophenyl)ethylene and the corresponding (carboranyl-methyl)styrene derivatives to give **Me-TDSE** and **Ph-TDSE**. Both compounds show similar absorption spectra and emission spectra, with two absorption bands at 340 nm and 409 nm and an emission band at 563 nm; that is, bands that are considerably redshifted and much more unstructured than those for stilbene. The changes in the optical spectra were conveniently rationalized by TD-DFT calculations, showing a considerable extent of conjugation, as well as a significant twist of the stilbene units at the TPE cores. The TDSE compounds are quite luminescent (Φ_F = 12–15 %), much more than the parent TPE (Φ_F < 1 %); this is ascribed to effective reduction of the internal conversion (IC), which might be due to the restriction of the conformational space, as well as to enhanced conjugation. In those suspension samples obtained in a mixture THF/H$_2$O (1:1000), the emission wavelengths are essentially unchanged against solution, due to the effective separation of neighboring π-systems through the space-filling character of the TDSE compounds; nevertheless, bright fluorescence was observed with higher quantum yields (Φ_F = 51–56 %), which is ascribed to further reduction of the IC process in a motion-restricted environment.

Experimental Section

General Procedures and Materials: All reactions were performed under dinitrogen employing standard Schlenk techniques. Toluene was purchased from Merck and distilled from sodium/benzophenone prior to use. Commercial-grade tetrahydrofuran and methanol were used without further purification. Compounds **1** and **2** were obtained according to a literature procedure,[6f] as was the synthesis of tetrakis(p-bromophenyl)ethylene (TBPE).[26] [Pd$_2$(dba)$_3$] and [Pd(tBu$_3$P)$_2$] were purchased from Aldrich, and NCy$_2$Me was purchased from Acros. The suspensions were prepared by adding **Me-TDS** and **Ph-TDS** solutions (5 μL, 10^{-3} M in THF) to water (5 mL), whilst stirring, and by continuing the stirring for a further 10 min.[21c]

Instrumentation: Elemental analyses were performed with a Carlo Erba EA1108 microanalyzer. ATR-IR spectra were recorded with a

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high-resolution spectrometer FTIR Perkin–Elmer Spectrum One. The ^1H NMR (300.13 MHz), ^{11}B NMR (96.29 MHz), and $^{13}C\{^1H\}$ NMR (75.47 MHz) spectra were recorded with a Bruker ARX 300 spectrometer. All NMR spectra were recorded at 25 °C, with samples in CDCl$_3$. Chemical-shift values for ^{11}B NMR spectra were referenced to external BF$_3$•OEt$_2$, and those for ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were referenced to SiMe$_4$. Chemical shifts are reported in ppm downfield from the reference, and all coupling constants are reported in Hz. UV/Vis absorption spectra were performed in spectroscopic-grade THF solution (Sigma–Aldrich) with concentrations of ca. 1×10^{-6} M in normal quartz cuvettes, with 1 cm optical path lengths. Absorption spectra of both solution and solid-state samples were measured by a Varian Cary-50 Bio UV/Visible spectrometer after proper baseline correction. Fluorescence emission and excitation for both the THF solution and aggregate suspension in THF/water (1:1000) were performed with a Fluoromax-4 spectrophotometer (Horiba), equipped with a xenon high-pressure lamp source and double monochromators for excitation and emission. The emission (λ_{exc} = 340 nm) and excitation spectra (Figures S4 and S5) were corrected for the wavelength sensitivity of the PMT and the excitation source, respectively. For display in the energy scale, the emission spectra were λ^2-corrected for constancy of the integrated area. Fluorescence quantum yields were determined by relative measurements (emissions integrated in the range 425–650 nm, λ_{exc} = 340 nm) against quinine sulfate (0.5 M H$_2$SO$_4$) with Φ_F = 0.55 (emission integrated in the range 380–580 nm, λ_{exc} = 347 nm).[27] For the suspensions in THF/water (1:1000), the refractive index was assumed to be that of water. Time-resolved fluorescence-lifetime measurements were done by using the time-correlated single-photon counting (TCSPC) technique, with an Acton SP2500 spectrometer and low-dark-current photomultiplier (PMA 06, PicoQuant) for detection. A HydraHarp-400 TCSPC event timer with 1 ps time resolution was used to measure the fluorescence decays. The excitation source was a 337 nm NanoLED (PicoQuant, PLS-8-2-651; 0.5 μW; trigger level 10 MHz at 90 % intensity) with FWHM (full width at half maximum) ca. 250 ps. The decay-time data was fitted after deconvolution with the IRF data by Fluofit software (Pico-Quant).

Calculations: Geometries of the ground and relevant electronic excited states of TDSE were calculated at the (TD-)DFT level of theory, imposing D_2 symmetry and using the B3LYP functional and 6-311G* basis set, as described in the Gaussian 09 package.[28] Molecular-orbital topologies were generated with Molekel.[29]

Synthesis of Me-TDSE: A 5 mL round-bottomed flask under nitrogen was charged with tetrakis(4-bromophenyl)ethylene (50 mg, 0.077 mmol), [Pd(tBu$_3$P)$_2$] (2 mg, 0.004 mmol), [Pd$_2$(dba)$_3$] (2 mg, 0.002 mmol), and 1-[CH$_2$C$_6$H$_4$-4′-(CH=CH$_2$)]-2-CH$_3$-1,2-$closo$-C$_2$B$_{10}$H$_{10}$ (**1**) (89 mg, 0.325 mmol). The solids were dissolved in dry toluene (2.5 mL), followed by the addition of NCy$_2$Me (0.15 mL, 0.679 mmol), and were stirred at 80 °C overnight. The reaction mixture was filtered through Celite, washed with THF (15 mL), and the solvent was removed under vacuum. The oily residue was dissolved in THF (1 mL), then CH$_3$OH (10 mL) was added, and the precipitated solid was filtered and washed with CH$_3$OH (15 mL), giving an intense-yellow solid, identified as **Me-TDSE**. Yield: 68 mg, 62 %. ^1H NMR (CDCl$_3$): δ = 7.46 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.31 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.17 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.09 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.06 (s, 8 H, CH=CH), 3.47 (s, 8 H, CH$_2$), 2.18 (s, CH$_3$) ppm. $^1H\{^{11}B\}$ NMR (CDCl$_3$): δ = 7.46 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.31 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.17 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.09 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.06 (s, 8 H, CH=CH), 3.47 (s, 8 H, CH$_2$), 2.29 (br., B-H), 2.21 (br., B-H), 2.18 (s, 12 H, CH$_3$), 2.10 (br., B-H) ppm. ^{11}B NMR (CDCl$_3$): δ = –5.74 (d, $^1J_{B,H}$ = 150 Hz, 8 B), –10.43 (d, $^1J_{B,H}$ =

133 Hz, 32 B) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ = 143.30 (s, C=C), 137.24 (s, C$_6$H$_4$), 135.49 (s, C$_6$H$_4$), 134.22 (s, C$_6$H$_4$), 131.90 (s, C$_6$H$_4$), 130.67 (s, C$_6$H$_4$), 129.11 (s, C$_6$H$_4$), 127.77 (s, CH=CH), 126.57 (s, C$_6$H$_4$), 126.09 (s, C$_6$H$_4$), 74.83 (s, C_c), 41.00 (s, CH$_2$), 23.68 (s, C_c-CH$_3$) ppm. ATR-IR: $\tilde{\nu}$ = 3025 (str, C$_{aryl}$–H), 2576 (str, B–H), 1604 (str, C=C), 1512, 1436 (str, C$_{aryl}$=C$_{aryl}$) cm^{-1}. C$_{74}$H$_{100}$B$_{40}$ (1422.00): calcd. C 62.50, H 7.09; found C 62.71, H 7.03.

Synthesis of Ph-TDSE: The procedure was the same as that for **Me-TDSE**, but using tetrakis(4-bromophenyl)ethylene (50 mg, 0.077 mmol), [Pd(tBu$_3$P)$_2$] (2 mg, 0.004 mmol), [Pd$_2$(dba)$_3$] (2 mg, 0.002 mmol), 1-[CH$_2$C$_6$H$_4$-4′-(CH=CH$_2$)]-2-C$_6$H$_4$-1,2-$closo$-C$_2$B$_{10}$H$_{10}$ (**2**) (107 mg, 0.318 mmol), and NCy$_2$Me (0.15 mL, 0.679 mmol). After precipitation, **Ph-TDSE** was obtained as an intense-yellow solid. Yield: 98 mg, 76 %. ^1H NMR (CDCl$_3$): δ = 7.73 (d, $^3J_{H,H}$ = 6 Hz, 8 H, C$_6$H$_5$), 7.50 (m, 12 H, C$_6$H$_5$), 7.35 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.28 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.07 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.01 (s, 8 H, CH=CH), 6.80 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 3.10 (s, CH$_2$) ppm. $^1H\{^{11}B\}$ NMR (CDCl$_3$): δ = 7.73 (d, $^3J_{H,H}$ = 6 Hz, 8 H, C$_6$H$_5$), 7.50 (m, 12 H, C$_6$H$_5$), 7.35 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.28 (d, $^3J_{H,H}$ = 9 Hz, C$_6$H$_4$), 7.07 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 7.01 (s, 8 H, CH=CH), 6.80 (d, $^3J_{H,H}$ = 9 Hz, 8 H, C$_6$H$_4$), 3.10 (s, CH$_2$), 2.73 (br., 8 H, B-H), 2.41 (br., 10 H, B-H), 2.31 (br., 8 H, B-H), 2.23 (br., 14 H, B-H) ppm. ^{11}B NMR (CDCl$_3$): δ = –3.75 (d, $^1J_{B,H}$ = 101 Hz, 8 B), –10.33 (d, $^1J_{B,H}$ = 103 Hz, 32 B) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ = 143.25 (s, C=C), 136.97 (s, C$_6$H$_4$), 135.48 (s, C$_6$H$_4$), 134.45 (s, C$_6$H$_4$), 131.88 (s, C$_6$H$_4$), 131.51 (s, C$_6$H$_5$), 130.87 (s, C$_6$H$_4$), 130.39 (s, C$_6$H$_5$), 129.04 (s, C$_6$H$_5$), 128.89 (s, C$_6$H$_4$), 127.86 (s, CH=CH), 126.34 (s, C$_6$H$_4$), 126.04 (s, C$_6$H$_4$), 83.71 (s, C_c-C$_6$H$_5$), 82.08 (s, C_c-CH$_2$), 40.74 (s, CH$_2$) ppm. ATR-IR: $\tilde{\nu}$ = 3025 (str, C$_{aryl}$–H), 2575 (str, B–H), 1603 (str, C=C), 1512, 1446 (str, C$_{aryl}$=C$_{aryl}$) cm^{-1}. C$_{94}$H$_{108}$B$_{40}$ (1670.29): calcd. C 67.59, H 6.52; found C 67.96, H 6.48.

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Luminescent Materials

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Tetrakis{[(*p*-dodecacarboranyl)meth-yl]stilbenyl}ethylene: A Luminescent Tetraphenylethylene (TPE) Core System

R = Me or Ph

366 nm → ~ 560 nm

Φ_F (NPs) > 50 %
Φ_F (solution) ~ 15 %
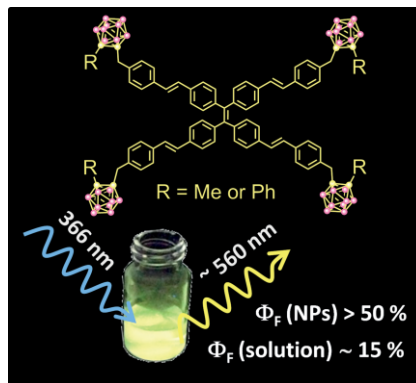
The tetrakis{[(*p*-dodecacarboranyl)-methyl]stilbenyl}ethylenes show significantly redshifted and enhanced emission compared with stilbene and tetraphenylethylene. Both effects can be traced back to enhanced conjugation, and emission enhancement is further promoted by the effective reduction of internal conversion through the restriction of conformational space.