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(Deep) Blue Through-Space Conjugated TADF Emitters Based on [2.2]Paracyclophanes

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Accepted 00th January 20xxEduard Spuling,^{‡a} Nidhi Sharma,^{‡b,c} Ifor D. W. Samuel,^{c*} Eli Zysman-Colman,^{b*} and Stefan Bräse^{a,d*}

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The first examples of through-space conjugated thermally activated delayed fluorescence (TADF) emitters based on a [2.2]paracyclophane (PCP) skeleton with stacked (coplanar) donor-acceptor groups have been synthesized. The optoelectronic properties are studied by the relative configuration, *cis* (pseudo-*geminal*) and *trans* (pseudo-*para*), of the donor and acceptor groups.

Thermally activated delayed fluorescence (TADF) is now regarded as the most promising mechanism for harvesting excitons¹ in electroluminescent devices and has thus garnered much attention in organic light-emitting diode (OLED) research following the seminal works of Adachi *et al.*²⁻⁵ A small energy gap (ΔE_{ST}) between the singlet and triplet excited states permits rapid effective equilibration between the two via intersystem crossing (ISC) and reverse intersystem crossing (rISC), evidenced by an observed thermally promoted delayed fluorescence upon photo- or electrical excitation.^{1, 6} A small ΔE_{ST} is achieved through a small exchange integral between frontier molecular orbitals; however, this has the potential to compromise the photoluminescence quantum yield (Φ_{PL}) by reducing the oscillator strength of the transition. Therefore, strict design principles must be followed to produce bright and efficient TADF emitters.⁷ Although the vast majority of reported TADF emitters adhere to the design paradigm of molecules containing donors and acceptors possessing a highly twisted relative conformation in order to minimize the exchange integral,

recent findings indicate that planar structures can exhibit TADF as well while maintaining a strong oscillator strength.^{8, 9} These examples demonstrate that the mechanism of and design rules governing TADF are still ripe for continuing investigation.¹⁰ Another striking design concept for TADF that has been explored by Swager, Baldo *et al.* is the electronic communication of donor and acceptor groups mediated by through-space conjugation either using a triptycene skeleton confining the donor and acceptor units in a 120° orientation,¹¹ or a xanthene-linked cofacial disposition of donor (D) and acceptor (A) with a distance of 3.3–3.5 Å.¹² Although TADF was observed with delayed lifetimes, τ_D between 2.0–3.0 μ s and moderate Φ_{PL} in this latter report, the through-space electronic communication mainly occurred via C–H \cdots π interactions, creating efficient aggregation induced emission.

The [2.2]paracyclophane (PCP) is a compact skeleton confining two benzene rings (“decks”) by ethylene bridges in a coplanar, though slightly bent and configurationally stable, conformation with a deck distance of 3.09 Å,¹³ which is smaller than the van der Waals distance between layers of graphite (3.35 Å). This enables a stronger transannular electronic communication between the benzene decks. This model compound for π – π transannular interaction sparked numerous investigations over the last decades. For instance, Bazan *et al.* investigated D–A stilbene derivatives based on PCP that exhibited nonlinear optical properties and significant through-space charge transfer,^{14, 15} including strong positive solvatochromism caused by a polarizable electronic structure in the excited state.¹⁶ Morisaki, Chujo *et al.* focused on PCP-based through-space π -extended conjugated polymers, demonstrating that electronic interactions can be effective through more than ten layers in the ground state, yet emission in these systems occurs from the isolated monomer π systems, giving access to well-defined monomer-localized HOMO-LUMO gaps rather than a broad valence-conduction band gap in the polymers.^{17, 18} Additionally, given the inherent planar chirality in PCPs, this scaffold can yield chromophores with intense circular polarized luminescence.¹⁹⁻²² Despite these fascinating properties, PCP chemistry suffers

^a Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany. Fax: (+49)-721-6084-8581; phone: (+49)-721-6084-2903; E-mail: braese@kit.edu

^b Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK. E-mail: eli.zysman-colman@st-andrews.ac.uk; Web: <http://www.zysman-colman.com>; Tel: +44 (0)1334 463826

^c Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, KY16 9SS, U.K. E-mail: idws@st-andrews.ac.uk

^d Institute of Toxicology and Genetics, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

[‡] These authors contributed equally to this work.

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from challenging or sometimes unpredictable reactivity. Although various successful cross-coupling protocols have been reported,²³ a direct C-N coupling to a *N*-heterocycle such as carbazole (Cz) or diphenylamine (DPA), though claimed in numerous patents,^{24,25} has never been reported in the scientific literature thus far.

In this communication we report the first examples of thermally activated delayed fluorescence enabled by through-space conjugation of a [2.2]paracyclophane skeleton (Fig. 1).

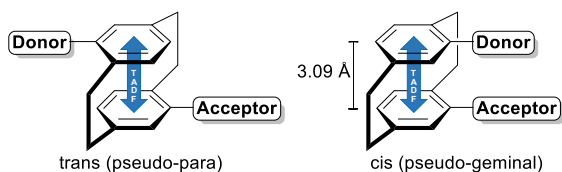
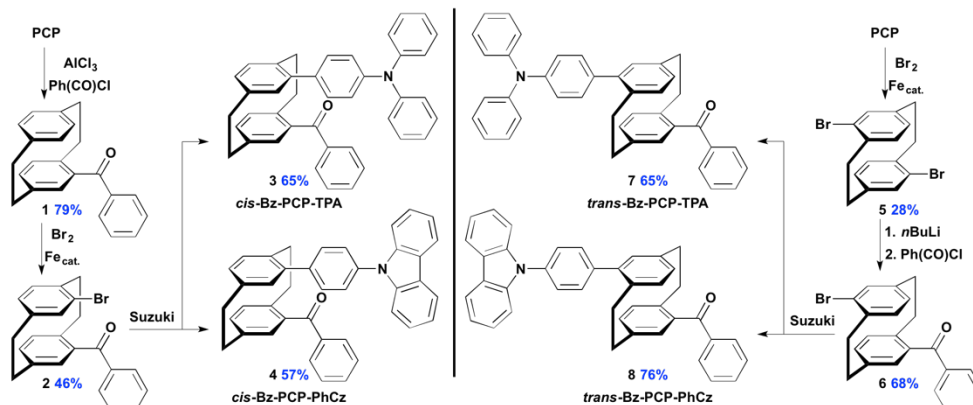


Figure 1 Concept of through-space conjugation of a [2.2]paracyclophane skeleton for thermally activated delayed fluorescence (TADF).



Scheme 1 [2.2]paracyclophane (PCP) based through-space conjugated benzoyl acceptor TADF systems. Left: Synthesis of pseudo-geminal (*cis*) TADF systems. Right: Synthesis of pseudo-*para* (*trans*) TADF systems. All molecules were prepared in a racemic fashion.

Density functional theory (DFT) calculations were performed in the gas phase to assess the electronic structures of both *cis* and *trans* derivatives (see ESI for details). The S_1 and T_1 excited states were calculated from the optimized ground state structure using the Tamm-Dancoff approximations^{30,31} (TDA) to TD-DFT. Focusing on the DPA derivatives, Fig. 2, the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for **3** and **7** are mainly localized over the donor and acceptor moieties and the adjoining benzene deck, respectively. The strong transannular electronic communication mediated by the PCP core promotes an efficient through space intramolecular charge transfer (ICT) while the inherent rigidity of the PCP was expected to minimize the vibrational motion of the molecule thereby reducing non-radiative decay pathways. The well separated frontier orbitals resulted in small calculated ΔE_{ST} values of 0.04 eV and 0.19 eV for **3** and **7**, respectively, coupled with high excited singlet energies (S_1 state), suggesting their strong potential as deep blue TADF emitters. Upon changing the donor group to the weaker carbazole, relatively large ΔE_{ST} values of 0.32 eV and 0.46 eV for isomers **4** and **8**, respectively, were observed (Fig. S2). No further studies were carried out for isomer **4** and **8**.

In order to obtain both the *cis* and *trans* isomers (pseudo-geminal and pseudo-*para* in PCP terminology, see Figure S1), two different approaches were investigated (Scheme 1). Compound **2** was synthesized by Friedel-Craft acylation of PCP and subsequent exploitation of the transannular directing effect to selectively target the pseudo-geminal position of the carbonyl group towards electrophilic aromatic bromination.²⁶ The *trans* (pseudo-*para*) intermediate **6** was obtained by monolithiation¹⁴ of the highly insoluble pseudo-*para* dibromide **5** followed by quenching with benzoyl chloride²⁷⁻²⁹. The intermediates **2** and **6** possess benzoyl acceptor groups²⁷⁻²⁹ and a bromo-functionalized building block suitable for cross-coupling of various donor groups. Targeting deep blue emitters, relatively weak donors (4'-*N,N*-diphenylamino)phenyl and (4'-*N*-carbazolyl)phenyl were installed via optimized Suzuki-Miyaura protocols (ESI) in moderate to good yields.

Figure 3a shows the UV-Vis absorption and photoluminescence (PL) spectra of **3** and **7** in toluene and the data are summarized in Table 1. Both isomers possess a high intensity absorption band at 311 nm, which was assigned to the ICT transition from D to A through the PCP based on TD-DFT calculations (Fig. S4).

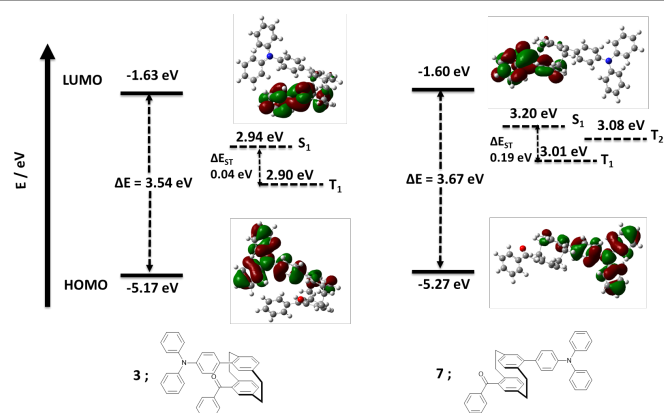


Figure 2. HOMO-LUMO profiles and excited state dynamics of *cis* and *trans* isomers **3** and **7**, respectively (pbe0/6-31G(d,p)).

In the PL spectra in PhMe, both isomers exhibited two distinct bands. The high energy band centred at 410 nm and 404 nm for **3** and **7**, respectively, was assigned to the “phane state” formed between two benzene decks of PCP scaffold.^{32, 33} The low energy band at 492 nm for **3** and 455 nm for **7** was attributed to the ICT transition between donor and acceptor moieties. Photoluminescence quantum yields, Φ_{PL} , in PhMe for **3** and **7** were 45% and 60%, which decreased to 30% and 42%, respectively, upon exposure to air. Time-resolved PL spectra (Fig. S1), however, do not show a delayed emission lifetime component, which would suggest that the TADF mechanism in solution is either not present or very weak.

We next investigated the solid-state PL behaviour of both derivatives in doped thin films (Fig. 3b). In the thin film, both derivatives exhibited an unstructured emission profile, characteristic of an excited state with significant ICT character.

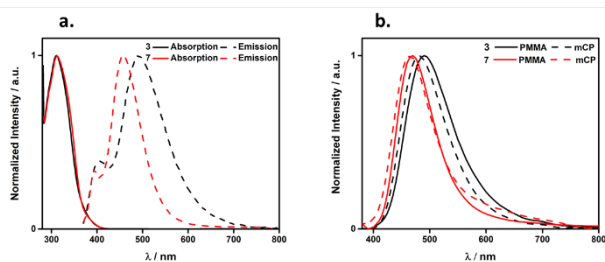


Figure 3. a.) UV-Vis and PL spectra in degassed PhMe and b.) PL spectra in 10 wt.% doped films in PMMA and 15 wt.% doped films in mCP of **3** (black) and **7** (red). $\lambda_{\text{exc}} = 360$ nm.

In 10 wt.% doped solution-processed films in PMMA, **3** showed sky-blue emission with λ_{PL} of 485 nm while the emission of **7** was slightly blue-shifted at 470 nm in strong agreement with the calculated S_1 energies. Both isomers exhibited a prompt lifetime, τ_{p} , of 19 ns (for **3**) and 10 ns (for **7**), followed by a very short delayed component, τ_{D} of 0.7 μs and 1.6 μs for **3** and **7**, respectively. However, the Φ_{PL} of the PMMA films of both the isomers remained low, close to 5% for **3** and 7.5% for **7**. With a view to employing these compounds as emitters in OLEDs, we next studied the emitters in the high triplet energy host, 1,3-bis(*N*-carbazolyl)benzene, mCP, with a vacuum-deposited doping concentration of 15 wt.%. The emission maxima were slightly blue-shifted at 480 and 465 nm for **3** and **7**, respectively, with strongly reduced Φ_{PL} of 12 and 15%, respectively, compared to solution-state measurements. Reducing the doping concentration to 1 wt.% resulted in reduced Φ_{PL} of 7% for both isomers (Table S1). The optoelectronic properties of **3** and **7** are influenced by the relative configuration of D and A. A red-shift in the emission spectra was observed for the *cis* isomer **3** across all media compared to **7**. This behaviour implies that the electronic coupling between D and A is stronger in the *cis* configuration than that in the *trans* configuration, likely a function of secondary π - π interactions in the former.

The ΔE_{ST} of **3** and **7** were determined from the singlet and triplet energies estimated from the onset of the prompt and delayed emission spectra, respectively, measured in 15 wt.% mCP doped films at 77 K (Fig 4). Both isomers exhibited high singlet energies coupled with small ΔE_{ST} values of 0.13 eV and 0.17 eV for **3** and **7**, respectively, confirming their TADF character.

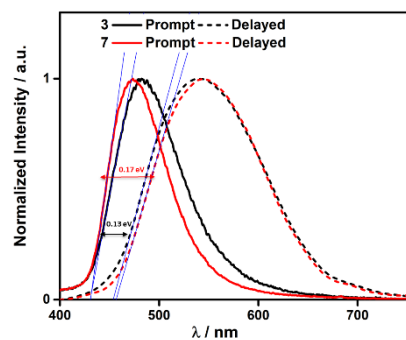


Figure 4. Prompt and delayed (by 50 μs , 200 μs window) spectra of **3** and **7** in 15 wt.% mCP doped films, measured at 77 K. ($\lambda_{\text{exc}} = 378$ nm)

Transient PL measurements in 15 wt.% mCP doped films revealed biexponential decay kinetics. Both isomers exhibited a prompt lifetime, τ_{p} , of 17 ns (for **3**) and 7.4 ns (for **7**) and a very short delayed lifetime, τ_{D} , of 1.8 μs (for **3**) and 3.6 μs (for **7**). Furthermore, rates of reverse intersystem crossing, k_{rISC} were found to $7.0 \times 10^5 \text{ s}^{-1}$ and $3.1 \times 10^5 \text{ s}^{-1}$ for **3** and **7**, respectively (Table S2, ESI). Such short τ_{D} and large k_{rISC} values are characteristics of an efficient rISC mechanism. Despite the desirable blue emission and short delayed lifetimes, the Φ_{PL} of these emitters remained poor. We investigated a range of high-energy host materials, such as DPEPO and CzSi, and doping concentrations (from 1-25 wt.%) in an effort to enhance the Φ_{PL} in the solid state; however, the highest Φ_{PL} values were found in mCP at 15 wt.% (Table S1).

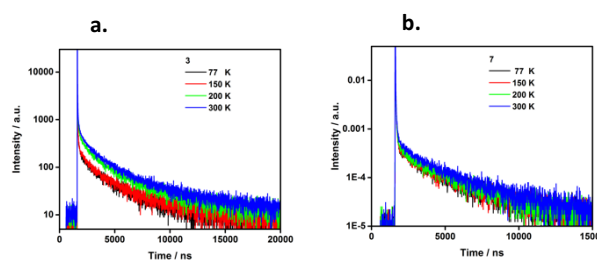


Figure 5. Temperature dependence of delayed lifetime of a.) **3** and b.) **7**. $\lambda_{\text{exc}} = 378$ nm.

To further corroborate the TADF nature of these emitters, we investigated the temperature dependence of the delayed lifetimes (Fig. 5). For both compounds, the intensity of delayed emission gradually increases with increasing temperature, providing direct evidence of TADF.

Table 1. Photophysical properties of **3** and **7**.

$\lambda_{\text{abs}}^{\text{a}}$ / nm	$\lambda_{\text{PL}}^{\text{a}}$ / nm	$\Phi_{\text{PL}}^{\text{b}}$ / %	$\Phi_{\text{PL}}^{\text{c}}$ / %	$\tau_{\text{p}}^{\text{d}}$ / ns	$\tau_{\text{D}}^{\text{d}}$ / μs

3 (cis)	311	480	45 (30)	12	17 (0.88)	1.8 (0.12)
7 (trans)	312	465	60 (42)	15	7.4 (0.44)	3.6 (0.56)

^a In degassed PhMe at 298 K. ^b 0.5 M quinine sulfate in H₂SO₄ (aq) was used as the reference (Φ_{PL} : 54.6%, λ_{exc} : 360 nm).³⁴ Values quoted are in degassed solutions, which were prepared by three freeze-pump-thaw cycles. Values in parentheses are for aerated solutions, which were prepared by bubbling air for 10 min. ^c Thin films were prepared by vacuum depositing 15 wt.% doped samples in mCP and values were determined using an integrating sphere (λ_{exc} : 360 nm); degassing was done by N₂ purge. Values in parentheses are the pre-exponential weighting factors, determined in 15 wt.% mCP doped films of **3** and **7** (λ_{exc} : 378 nm).

In conclusion, we have developed the first examples of TADF emitters incorporating a **PCP** core, which we exploited to mediate electronic communication between donor and acceptor groups on adjoining benzene decks. Both the *cis* and *trans* isomers exhibited blue TADF emission and short delayed lifetimes in the range of 1–3 μ s. These compounds unfortunately possess low photoluminescence quantum yields in the solid state. We are presently investigating modified designs to mitigate this issue such that paracyclophane-based TADF emitters can be incorporated into OLED devices.

Conflicts of interest

There are no conflicts to declare.

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