Donor-Acceptor Iptycenes with Thermally Activated Delayed Fluorescence

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<td>As Published</td>
<td><a href="http://dx.doi.org/10.1002/ejoc.201700703">http://dx.doi.org/10.1002/ejoc.201700703</a></td>
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<tr>
<td>Publisher</td>
<td>Wiley Blackwell</td>
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<tr>
<td>Version</td>
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<td>Accessed</td>
<td>Thu Dec 13 21:16:00 EST 2018</td>
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**Donor-Acceptor Iptycenes with Thermally Activated Delayed Fluorescence**


**Abstract:** A new donor-acceptor iptycene containing carbazole donors and a thiadiazoloquinoxaline acceptor was synthesized and its photo- and electrochemical properties evaluated. The key intermediate 1 allows for a lateral modification through cross-coupling and the (trisopropylsilyl)acetylene product 2 exhibits bright yellow fluorescence with emission lifetimes of 2.42 ms in deoxygenated hexane. The long lifetime and high quantum efficiency (73%) is quenched by O₂ and therefore attributed to thermally activated delayed fluorescence (TADF). This approach allows functionalization through cross-coupling reactions and depicts a promising scaffold for the synthesis of TADF-active molecules.

**Introduction**

There has been extensive research into OLED technologies from academia and industry in recent years, as a result of the advantages over traditional liquid crystal displays such as flexibility,[8] higher contrast ratio, and ease of manufacturing.[9] However, there is an inherent drawback with fluorescent organic materials in that singlet and triplet excitons are obtained in a 1:3 statistical ratio upon electrochemical excitation.[10] Since only the radiative decay from the singlet state is spin-allowed, the internal electroluminescent quantum efficiency (ηel) is limited to 25%. Heavy metal luminescent complexes containing iridium or platinum circumvent this issue through efficient spin-orbit coupling and have been shown to achieve ηel of virtually 100%.[14,15] Phosphorescent organometallic materials have therefore played a vital role in the development of OLED technologies but suffer from drawbacks including cost, element sustainability, stability of blue emitters, and triplet-triplet annihilation at high current densities causing quantum efficiency roll-off.[6] Delayed fluorescence and emission from the doublet state by stable emissive radicals have been proposed as two triplet harvesting alternatives.[7,8] Delayed fluorescence can also in principle be achieved through the up-conversion of triplet excitons to singlet excitons by triplet-triplet annihilation (TTA).[9] Hybridized local charge transfer (HLCT) or thermally activated delayed fluorescence (TADF).[11–13] TADF tends to outperform the other delayed strategies and has recently been reported to achieve high emission efficiencies, thus rendering this approach a promising strategy to create efficient OLEDs.[14–16] In TADF materials, intersystem crossing is very fast allowing for the thermal equilibration of triplet and singlet excitons (Figure 1). This can be realized when the S₁ and T₁ states are close in energy because of the inverse proportionality between the singlet-triplet gap (ΔEST) and the first-order mixing coefficients.[17] Adachi and co-workers have pioneered TADF and have demonstrated that introducing a torsional angle between donor and acceptor groups results in largely segregated HOMO and LUMO states that lower the exchange energy and give rise to a small ΔEST.[15,18–23] Our group recently reported an alternative approach with which TADF can be achieved through homocoujugation in donor-acceptor triptycenes.[24] We initially chose the triptycene scaffold as a result of its inherent high thermal stability,[25,26] a vital factor in the OLED manufacturing process. We seek to expand this approach to materials that allow for a more diverse functionalization to modulate emission wavelength and realize higher quantum efficiencies.

![Figure 1. Competing photophysical processes from the excited state. isc = intersystem crossing, ris = reverse intersystem crossing. Excitons visualized as balls. Drawing inspired by Adachi and co-workers, Ref. 17.](image_url)

The design of new iptycene donor-acceptor structures utilizes known building blocks. We anticipated that carbazole, a strong donor that can be substituted with solubilizing alkyl side chains, can be paired with a thiadiazoloquinoxaline acceptor to produce a TADF material (Figure 2).
As shown in Figure 3, the HOMO and LUMO frontier orbitals are spatially well separated promoting a small $\Delta E_{ST}$ and enhanced $T_1 \rightarrow S_1$ reverse intersystem crossing. The HOMO is delocalized over the carbazole moieties whereas the LUMO is located on the thiazoloquinoxaline acceptor suggesting that the $S_1$ state has charge transfer character. Whilst heavy atoms are not required for an efficient spin conversion, we anticipated that the introduction of the sulfur atom in the thiazole moiety may still be favorable for higher intersystem crossing rates. Such processes are expected to enhance the interconversion of $T_1$ and $S_1$, and that the rigid framework minimizes non-radiative pathways from the excited states.

Having prepared 1 with two opposing aryl bromides allows numerous modifications through cross-couplings. We chose a Sonogashira coupling with (triisopropylsilyl)acetylene to yield 2 in 76% yield (Scheme 2). Compounds 1 and 2 were characterized by $^1$H and $^{13}$C NMR, and high resolution mass spectrometry.

With product 2 in hand, we were interested to evaluate its photophysical properties. We observed an absorption maximum at 478 nm with a pronounced shoulder peak at 508 nm in hexane (Figure 4), suggesting the expected charge transfer character. The compound is emissive with a maximum luminescence at 524 nm and a shoulder peak at 552 nm, manifested in a bright yellow emission. The preservation of the shoulder in the emission spectrum indicates that there is little reorganization in the excited state, presumably a result of the rigid framework. The Stokes shift of the $S_1$ state is relatively small compared to typical charge transfer states, indicating that the excitation involves a limited relaxation of the molecular geometry. We also noticed that the photoluminescence is sensitive to the polarizability of the solvent. In toluene, the emission is red-shifted by 76 nm ($\lambda_{em} = 600$ nm), whilst in ethanol the emission peak is located at 548 nm. These more polarizable solvents negatively affect the quantum yields, as also seen in other donor-acceptor iptycenes (Figure S11).

**Results and Discussion**

Our target core molecule, 1, was synthesized as shown in Scheme 1, starting with a Pd-catalyzed N-arylation of 3,6-dioctyl-9H-carbazole with 2,6-dibromoanthracene using XPhos as the ligand. Other conditions including different palladium sources, ligands or Ullmann coupling failed to do this transformation in reasonable yields. With the dicarbazoleanthracene intermediate in hand, the diketone structure was obtained by a Diels-Alder cycloaddition with vinylene carbonate, followed by a basic hydrolysis and a Swern oxidation, all proceeding in high yields. The final step consisted of the condensation with 4,7-dibromobenzo[c]1,2,5-thiadazole-5,6-diamine to form 1 in 90% yield.
To evaluate if this iptycene scaffold is TADF active, we sought out the effects of oxygen that quenches the long-lived triplet states and were looking for both a nanosecond scale prompt emission as well as a microsecond scale delayed component. The compound showed a high quantum yield of 73% in deoxygenated hexane, much higher than the previously reported homocoujugated triptynes from our group[24] that decreased to 43% after oxygen saturation. This observation suggests that there is a long-lived excited state that is quenched by oxygen indicative of TADF behavior. Time-resolved photoluminescence with a streak camera was employed (Figure 5) and the results show the expected microsecond response (2.42 µs lifetime), which disappears to a nanosecond emission lifetime after O₂ saturation (12.5 ns lifetime). Both findings are evidence that this molecule is indeed TADF active. It is furthermore noteworthy that higher concentrations quench the emission and that the relative peak heights change in favor of a longer wavelength emission at higher concentrations, indicating excimer formation (Figure S13). The absorption spectra are independent of concentration and therefore don't indicate the presence of aggregated species in the ground state (Figure S12).

The HOMO energy levels were estimated using cyclic voltammetry (Figure 6). Compound 2 displayed a reversible oxidation wave at 0.76 V (vs Fc/Fc⁺), which can be assigned to an oxidation of the carbazole moieties. The HOMO/LUMO levels were based on the oxidation potential and the onset of UV-vis absorption spectra and calculated as ~5.9–2.0 eV.

Conclusions

We have designed a high-yielding synthetic approach to the versatile intermediate 1 possessing a thiadiazoloquinoxaline acceptor, electron-rich iptycene wings and solubilizing alkyl chains. This privileged intermediate allows further functionalization using different cross-coupling partners due to two lateral aryl bromides. The (triisopropylsilyl)acetylene product 2 exhibits bright yellow fluorescence with emission lifetimes of 2.42 µs and a quantum yield of 73% in degassed hexane. The long lifetime is quenched by O₂ and is attributed to thermally activated delayed fluorescence (TADF).

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or CD₂Cl₂ solutions on a Bruker AVANCE 400 MHz or JEOL ECZ-500 spectrometer. The chemical shift data are reported in units of δ (ppm) relative to residual solvent. Ultraviolet-visible absorption spectra were measured with a Cary 4000 UV-Vis spectrophotometer from Agilent Technologies and corrected for background signal with a solvent filled cuvette. All electrochemical measurements were carried out with Autolab PGSTAT30 potentiostat (Eco Chemie B.V.) in a conventional three-electrode configuration system: a platinum working electrode (1.6 mm diameter), a platinum wire counter electrode and a silver wire in 0.01 mM silver nitrate in acetonitrile with 0.1 mM tBu4PF₆ as electrolyte in a porous vycor fritted electrode as pseudo-reference electrode with ferrocene added after every run as the internal standard. Dichloromethane was employed as the solvent with 0.1 M tBu4PF₆ (TBAPF₆) as the electrolyte and the experiments were performed under ambient condition with a scan rate of...
2.6-bis(3,6-dioctyl-9H-carbazol-9-yl)-11,12-diole: The dioleoxane (2.00 g, 1.92 mmol) was dissolved in 1,4-dioxiane (20 mL) and a 4M aqueous solution of sodium hydroxide (7 mL) was added.

The resulting mixture was, refluxed for 1.5 h. After cooling to ambient temperature the product was extracted using chloroform (3 x 50 mL).

Subsequently the combined organic layers were washed with aqueous NaHCO₃ (100 mL) and brine (50 mL). The crude product was obtained after drying over magnesium sulfate and evaporation of the solvent. Column chromatography (silica gel, hexane:CH₂Cl₂ 1:1) yielded the product as an off-white sticky solid (1.74 g, 1.71 mmol, 89%).

1H NMR (400.05 MHz, CDCl₃, 25 °C): δ = 7.94 (s, 2H), 7.65 (d, 1H, J = 2.2 Hz), 7.60 (d, 1H, J = 7.8 Hz), 7.57 (d, 1H, J = 2.2 Hz), 7.54 (d, 1H, J = 7.8 Hz), 7.47 (dd, 1H, J = 7.8 Hz, J = 2.2 Hz), 4.65-4.56 (m, 2H), 4.26 (s, 2H), 2.81 (t, 8H, J = 6.7 Hz), 2.45-2.36 (brs, 2H), 1.79-1.70 (m, 8H), 1.44-1.29 (m, 40H), 0.91 (t, 12H, J = 6.8 Hz); 13C [1H] NMR (100.60 MHz, CDCl₃, 25 °C): δ = 141.0, 139.9, 138.5, 138.3, 138.4, 135.8, 135.3, 132.7, 128.7, 128.6, 128.4, 128.2, 121.0, 120.1, 109.9, 109.8, 76.8, 76.7, 47.8, 48.2, 48.6, 36.5, 36.5, 32.9, 32.5, 30.2, 30.0, 29.9, 23.3.

2.6-bis(3,6-dioctyl-9H-carbazol-9-yl)-9,10-ethanoanthracene-11,12-dione: Trifluoroacetic anhydride (576 µL, 870 mg, 4.14 mmol) was added at -78 °C to a mixture of dry DMSO (329 µL, 362 mg, 4.63 mmol) and dry CH₂Cl₂ (22 mL) under argon and the resulting solution was stirred for 10 min.

A solution of the diole starting material (1.37 g, 1.35 mmol) in CH₂Cl₂/DMSO:2:1 (v/v) 10.5 mL was added within 15 min and the mixture was stirred for a further 60 min at -78 °C. Hünig's base (1.4 mL, 38.7 mmol) was added slowly. The reaction mixture was allowed to warm to room temperature and subsequently poured into 2M hydrochloric acid (200 mL). When the evolution of gas had stopped, the two layers were separated.

The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with water (50 mL) and dried over magnesium sulfate. The solvent was evaporated and the residue purified by flash column chromatography (silica gel, hexane:CH₂Cl₂ 1:1) to give the diketone as an orange solid (1.16 g, 1.18 mmol, 85%).

The product was used in the next step without characterization due to its instability in solution.

4,13-dibromo-8,17-bis(3,6-dioctyl-9H-carbazol-9-yl)-6,11-[1,2]benzenediol[2][1,2,5]thiadiazolo[3,4-j]phenazine (1): Iptycine quinone (975 mg, 962 mmol) and diamino benbazothiazole (405 mm, 1.25 mmol) were dissolved in acetic acid (10 mL) and chloroform (7 mL).

Upon heating to 80 °C the color changed to dark red as a consequence of product formation. After cooling to ambient temperature the reaction mixture was diluted with water and the product extracted with dichloromethane. The combined organic layers were washed with an aqueous solution of sodium carbonate and brine. After drying over MgSO₄ and evaporating under reduced pressure, flash column chromatography (silica gel, hexane:CH₂Cl₂ gradient of 3:1 to 1:1) gave the product as an amorphous red solid (1.12 g, 90%).

1H NMR (400.05 MHz, CDCl₃, 25 °C): δ = 7.94 (2H, J = 2.0 Hz), 7.89 (2H, J = 7.8 Hz), 7.82 (4H, J = 1.0 Hz), 7.47 (dd, 2H, J = 7.8 Hz, J = 2.0 Hz), 7.21 (dd, 4H, J = 8.6 Hz), 7.09 (dd, 4H, J = 8.6 Hz, J = 1.5 Hz), 6.00 (s, 2H), 2.76 (t, 8H, J = 7.7 Hz), 1.73-1.64 (m, 8H), 1.41-1.24 (m, 40H), 0.91-0.84 (m, 12H); 13C [1H] NMR (100.60 MHz, CDCl₃, 25 °C): δ = 158.6, 152.3, 142.3, 139.5, 138.7, 138.1, 135.1, 127.1, 126.8, 126.3, 124.2, 123.8, 119.8, 119.4, 110.9, 105.4, 36.2, 32.5, 32.2, 29.8, 23.9, 22.9, 14.4. HRMS (ESI) m/z: [M+H]+ Calculated for C₇₂H₄₃N₂O₂S₂: 1151.5235; Found: 1151.5253.

4,13-dibromo-8,17-bis(3,6-dioctyl-9H-carbazol-9-yl)-6,11-[1,2]benzenediol[2][1,2,5]thiadiazolo[3,4-j]phenazine (2): 1 (50 mg, 38.4 µmol), Pd(PPh₃)₄ (2.2 mg, 1.92 µmol) and Cul (0.4 mg, 1.92 µmol) were suspended in HMPA/THF (32 µL 0.3 mL) and degassed with argon for 15 minutes before triisopropoxyalicylene (37 mg, 88 µL, 380 µmol) was added and the resulting reaction mixture stirred at 45°C for 16 h. Upon completion, the reaction mixture was quenched with water and the product extracted with CH₂Cl₂, dried over MgSO₄ and the solvent evaporated under reduced pressure.

The crude product was purified by column chromatography (silica gel, hexane:CH₂Cl₂ 1:1) to give product 2 as a red solid (43 mg, 76%).

2H NMR (500 MHz, Methylene Chloride-d₄) δ 7.91 (s, 4H), 7.85 (d, J = 7.8 Hz, 4H), 7.48 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 8.3 Hz, 4H), 7.20 (dd, J = 8.4, 1.7 Hz, 4H), 5.79 (s, 2H), 2.77 (t, J = 7.7 Hz, 8H), 1.70 (p, J = 7.3 Hz, 8H), 1.29 (s, 90H), 0.87 (t, J = 6.7 Hz, 13H), 13C NMR (126 MHz, CDCl₃) δ 158.00, 154.53, 142.99, 141.58, 139.75, 139.54, 137.77, 135.23, 127.21, 126.99, 126.12, 124.04, 123.79, 119.86, 114.35, 109.72, 109.36, 101.33, 36.29, 32.73, 32.31, 30.08, 29.94, 29.75, 29.17, 18.99, 14.28. 11.93. HRMS (ESI) m/z: [M+H]+ Calculated for C₁₂₀H₁₁₁₃N₂O₃S₂: 1503.9698; Found: 1503.9692.

Acknowledgements
Financial support was provided through the Airforce Office of Scientific Research, and the German Research Foundation (DFG) of JUE.

**Keywords:** TADF • donor-acceptor • iptycene • Sonogashira • organic materials


A new donor-acceptor iptycene scaffold is reported, with the key intermediate product allowing facile lateral modification through cross-coupling. The (triisopropylsilyl)acetylene product is highly emissive in solution and we demonstrate that this material is TADF active.

TADF, OLEDs
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