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Iptycene-Containing Azaacenes with Tunable Luminescence

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Abstract An optimized route toward iptycene-capped, *p*-dibromoquinoxalinophenazine was developed, increasing the yield significantly from literature procedures. New iptycene-containing symmetrical azaacenes were synthesized from this intermediate using Suzuki–Miyaura cross-coupling, and their photophysical properties were evaluated. Tuning the substituents allows modulating emission wavelengths across the visible spectrum. Substitution with 3-methoxy-2-methylthiophene exhibits a quantum yield of 35%. The (triisopropylsilyl)acetylene product has a quantum yield of 38% and serves as a model compound for the synthesis of polymers based on this electrooptically active molecular motif.

Key words *N*-heteroiptycene, Suzuki–Miyaura cross-coupling, Sonogashira coupling, pyrazinoquinoxaline, luminescence

In recent years, there has been an immense interest in organic materials for OLEDs, OFETs, and PVs, encouraged by the ease of tunability through design and solubility compared to inorganic counterparts, which is conducive to large-scale printing techniques.^{1,2} OLEDs, as an example, initially struggled with efficiency because upon electrochemical excitation, singlet and triplet excitons are formed in a 1:3 statistical ratio.³ Since only the radiative decay from singlet excitons is quantum chemically fully allowed and the long-lived triplet excitons usually relax through nonradiative processes, internal electroluminescent quantum efficiency (η_{int}) of most organics is limited to 25%. Phosphorescent materials and delayed fluorescence have been investigated as triplet harvesting strategies. Most of these materials incorporate heavy metals and have been shown to achieve η_{int} values that are essentially 100%. However, their use is constrained by cost, the limited stability of blue emitters, and triplet-triplet annihilation at high current densities.⁴⁻⁶ Emissive stable radicals have also been considered, but there is currently only a limited number of structures suitable for this purpose and quantum efficiencies have thus far been low.^{7,8} Recently, high-emission efficiencies from thermally activated delayed fluorescence (TADF) have been reported, and this method is emerging as a promising approach to create efficient OLEDs.⁹ Indeed this method tends to outperform the up-conversion of triplets to singlet excitons by triplet-triplet annihilation.¹⁰⁻¹² TADF requires the energetic proximity of the S_1 and T_1 state and the first-order mixing coefficients between singlet and triplet states are inversely proportional to the singlet-triplet gap (ΔE_{ST}).¹³ This small ΔE_{ST} allows fast intersystem crossing for the thermal equilibration of triplet and singlet excitons. Electroluminescence with η_{int} approaching 100% have been realized through TADF.^{9,14} There are two classes of TADF materials that meet the electronic requirements of a low $\Delta E_{\text{st.}}$ A torsion angle between donor and acceptor moieties9,15,16 or having the donor-acceptor groups in homoconjugation, both provide mechanisms to produce segregated HOMO and LUMO states that lower the exchange energy and give rise the small energy difference.¹⁷ In fact, another promising approach for OLEDs and other optical applications involves the spatial segregation of FMOs. In this context we were interested in investigating cruciforms comprising two perpendicular π -conjugated linear units connected by a central aromatic core and thereby can reduce HOMO and LUMO orbital overlap.¹⁸⁻²²



Figure 1 Generic target structures targeted in this publication

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Scheme 1 Synthetic procedure for the synthesis of intermediate **7**

We postulated the generic structure shown in Figure 1 to display favorable optical properties. The electron-deficient pyrazinoquinoxaline core will have little HOMO–LUMO orbital overlap with a relatively bulky electron donor that is forced to adopt a twisted conformation.^{23,24} The three-dimensional structurally rigid iptycene wings minimize the typical tendency of azaacenes for π stacking that can lead to self-quenching and reduced quantum yields.^{25,26} The isolated phenyl groups of the iptycene wings are not expected to contribute significantly to the HOMO or LUMO.²⁷

We targeted a modular synthetic route for symmetric azaacenes and envisioned **7** as a valuable key intermediate because the lateral aryl bromides allow functionalization through cross-coupling reactions. The diketone intermediate **4** was synthesized as shown in Scheme 1, through adaptation of a literature procedure that involves Diels–Alder reaction of anthracene with vinylene carbonate, followed by a basic hydrolysis and a Swern oxidation.²⁸

The condensation of **4** was complicated by the fact that 3,6-dibromobenzene-1,2,4,5-tetraamine (6) is unstable and has to be prepared in situ. Literature procedures for the reduction of 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (5) followed by condensation to a diketone are generally low yielding (20% and 47% for related structures),^{29,30} and as a result we decided to optimize the reaction cascade. Following the established literature procedure provided 7 in 33% yield (Table 1, entry 2). Other reaction conditions such as varying the temperature, zinc activation by hydrochloric acid, increasing the amount of zinc, or the use of hydrochloric acid instead of acetic acid, did not increase the yield of the reaction (Table 1, entries 1, 3-6). Analysis of the reaction mixture revealed a considerable amount of residual diketone 4, thus encouraging the use of an excess of 5. Yields improved up to 65% when 1.38 equivalents of 5 were utilized (Table 1, entry 8).

Having the tetraamine **6** in excess, however, increases the likelihood of monocondensation, hence the order of addition was reversed. Slowly adding the amine to a solution of the diketone in acetic acid over one hour furthermore raised the yield to 72% (Table 1, entry 10). Despite the promising increase in yield, we encountered issues in scaling up the reaction, and diminished yields were observed at scales more than 60 mg of **4**.

Having optimized the first reaction cascade, we endeavored to introduce donor groups to **7** through cross-coupling reactions. We surveyed both Stille and Suzuki–Miyaura couplings and converged on the latter based upon higher yields whilst avoiding toxic tin reagents. Reaction optimization with (3,5-dimethoxyphenyl)boronic acid revealed that cross-coupling to **7** could be achieved in 99% yield using Pd₂(dba)₃/P(o-tol)₃ as the catalyst at 60 °C. Other catalysts such as Pd(PPh₃)₄, the addition of CuI, Pd-XPhos-G2, or Pd(dppf)Cl₂ resulted in low to moderate yields (Table 2).

The optimized reaction conditions were applied to a variety of (hetero)aryl boronic acids and the C–C cross-coupling products **9–13** could be obtained in yields ranging from 65–99% (Figure 2).

Table 1 Reaction Optimization for the Synthesis of 7

Entry	Temp (°C)ª	Activated zinc ^b	Acid	Zinc (equiv)	5 (equiv)	Yield (%)
1	50	No	AcOH	20	0.50	trace
2	60	No	AcOH	20	0.50	33°
3	70	No	AcOH	20	0.50	trace
4	60	Yes	AcOH	20	0.50	trace
5	60	No	HCI	20	0.50	trace
6	60	No	AcOH	200	0.50	trace
7	60	No	AcOH	20	1.25	61 ^c
8	60	No	AcOH	20	1.38	65°
9	60	No	AcOH	20	1.50	57°
10	60	No	AcOH	20	1.38	72 ^c

^a Temperature used for reduction of 5 to 6.

^b Zinc activation by HCl.

^c Isolated yield.



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^alsolated yield.

We furthermore attempted to extend the scope to include palladium-catalyzed *N*-arylation with carbazole in order to introduce stronger donors. Unfortunately, initial attempts using a variety of ligands (XPhos, *t*-BuBrettPhos, Ru-Phos, or *t*-BuXPhos) only produced unreacted and reduced forms of **7**. However, the *N*-arylation with iminodibenzyl, which is known to be a better nucleophile than carbazole,³¹ proceeded smoothly to give **14** in 56% yield using the Buchwald precatalyst Pd-RuPhos-G4 (Scheme 2).

These promising coupling results with aryl bromides also encouraged us to synthesize a (triisopropylsilyl)acetylene product **15** via a Sonogashira reaction catalyzed by Pd(PPh₃)₄ and Cul in 57% yield (Scheme 3). This compound serves as a model compound for a hypothetical acetylenelinked polymer of **7**. The yield of the Sonogashira reaction







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in this case is too low to be of utility for the synthesis of polymers, which require near quantitative yields. We note that **15** has very recently been synthesized by Bunz and co-workers through a different synthetic route.³²

We were interested to determine if these materials displayed desirable optical properties, including TADF. Representative absorption spectra of the compounds **9–13** are shown in Figure 3. All of the compounds display vibronic fine structure with peaks that are summarized in Table 3. The broad tails at longer wavelength are suggestive of charge-transfer character.

5x10 9 Aolar Absorptivity (L mol⁻¹ cm⁻¹) 10 4x10 11 12 13 3x10 2x104 1x10 0 300 250 350 400 450 500 Wavelength (nm) Figure 3 Absorption spectra with molar absorptivity for 9-13 in hex-

 Table 3
 Optical Properties of Compounds 9–15, Measured in Hexane

Compd	$\lambda_{max}(emis)$	QY (%)	$\lambda_{max}(abs)$
9	470	2.2·10 ⁻³	268, 300, 367, 385
10	478	0.06	268, 397, 368, 387
11	510	0.07	274, 303, 368, 386
12	586	0.35	248, 274, 309, 373, 397
13	608	0.11	266, 301, 374, 393
14	-	-	265, 360, 378, 400, 522
15	466, 495	0.29 (0.38) ^a	275, 307, 378, 400, 427, 454

^a Degassed by bubbling argon through solution.

ane

To determine if this class of compounds displays TADF behavior, we measured the quantum yields in both deoxygenated and oxygen-containing solvents. In TADF systems, triplet states contribute to a delayed component, which renders the compounds susceptible to quenching by oxygen.^{33,34} An increase in quantum yield in an oxygen-free solvent is therefore an indication of TADF. As shown in Figure 4, compounds **9–13** were emissive, however, saturating the solutions with oxygen did not significantly affect the quan-



Figure 4 Emission spectra of compounds 9–13 in hexane



Figure 5 Photophysical characterization of 15, measured in hexane

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tum yield, thereby suggesting that these compounds are not TADF active or have a sufficient lifetime because of rapid nonradiative processes. Compound **14**, which has a stronger donor in the iminodibenzyl group, was only weakly emissive as a result of a weak charge-transfer band (Figure S10). Nevertheless, the absorption and emission compounds produced impressively cover essentially the whole visible spectrum. The (triisopropylsilyl)acetylene product **15** shows several well-defined absorption maxima as shown in Figure 5. The compound is emissive with a maximum at 466 nm with a pronounced shoulder peak at 495 nm, to give a visibly green emission. The quantum yield was 38% in degassed hexane, but decreased to 29% after oxygen exposure. This suggests the presence of long-lived excited states, most likely triplet states, that are quenched by O_2 .



Figure 6 DFT calculations of HOMO and LUMO for compounds 8–15. The calculations were performed using the B3LYP functional and 6-31+G* basis set.

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We performed DFT calculations using the B3LYP functional and 6-31+G* basis set to evaluate the HOMO-LUMO separation of all of the products (Figure 6). They show, as anticipated, the iptycene wings do not contribute to either HOMO or LUMO states. The HOMO and LUMO frontier orbitals, however, have sizable overlap in products 9-11. The exchange energy that stabilizes the triplet is therefore significant and produces a larger ΔE_{st} that decreases the coupling between the singlet and triplet states and reduces the reverse intersystem crossing (RISC). This is consistent with the experimental data that the aryl-substituted products are TADF inactive. Our DFT calculations suggest that products 8, 12, and 13 seem to have favorable spatial HOMO-LUMO separation that provides only minor orbital overlay and at the onset we expected these compounds to be TADF active. However, these are gas phase, ground state, calculations with equilibrium conformations. It is possible that in the excited-state conformations and dynamics are present that promote larger ΔE_{st} and competitive nonradiative relaxations. With regard to the latter, the quantum yields of these materials are modest to low. The TIPS acetylene product 15 shows high overlap between the HOMO and LUMO states. This is inconsistent with TADF behavior. This effect may be the result of the silicon groups, however, conformation of the origin of the intersystem crossing will require additional investigations that are beyond our initial synthetic studies that are the focus of this publication.

In conclusion, we report the synthesis of **7** through an optimized synthetic route.³⁵⁻³⁹ The in situ reduction of 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole was optimized to boost the yield to 72%. The versatility of the dibromoaryl intermediate **7** was exemplified in a variety of Suzuki-Miyaura cross-coupling reactions that proceed in moderate to excellent yields (65–99%), a palladium-catalyzed *N*-arylation with iminodibenzyl, and a Sonogashira reaction with (triisopropylsilyl)acetylene. Most of the products are luminescent with emission colors ranging from blue to orange. We anticipate this molecular scaffold could potentially be used to create new materials with useful electrooptical properties.

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Supporting Information

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- (35) **Preparation of Compounds 2 and 3** Following a literature procedure, see ref. 21.

(36) **Preparation of Compound 7**

The optimized reaction was carried out in a 20 mL vial, containing zinc powder (470 mg, 7.19 mmol) suspended in AcOH (3.5 mL). Under stirring compound 5 (138 mg, 358 µmol) was added, and the reaction mixture was heated to 60 °C for 1 h. The reduced colorless intermediate 6 was separated from the zinc powder by filtration through a pad of Celite and added dropwise to a solution of 4 (61 mg, 260 µmol) in AcOH (1.5 mL) over 1 h. A yellow precipitate immediately formed. The solution was stirred for another 1 h and extracted several times with CH₂Cl₂ (20 mL) until the organic phase was colorless. The combined organic layers were washed with an aq NaHCO₃ solution (100 mL) and water (100 mL). After evaporation of the solvent, the crude product was purified via column chromatography (SiO₂, hexane-CH₂Cl₂ = $3:1 \rightarrow 0:1$). The product (7, 65 mg, 93.8 µmol, 72%) was obtained as a yellow powder. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 7.59 (dd, J3 = 5.4 Hz, J4 = 3.2 Hz, 4 H, CH), 7.17 (dd, J3)$ = 5.4 Hz, J4 = 3.2 Hz, 4 H, CH), 5.84 (s, 4 H, CH) ppm.

(37) Preparation of Compounds 8–13 (GP1)

A Schlenk flask was filled with **7** (10 mg, 14.4 µmol), arylboronic acid (2.2 equiv, 31.7 µmol), and K_3PO_4 (12.3 mg, 57.8 µmol), evacuated, and purged with argon. A mixture of water-toluene–1,4-dioxane (1:1.8:5.5, 0.5 mL) was added, and the resulting suspension degassed with argon for 15 min. Subsequently, $Pd_2(dba)_3$ (0.4 mg, 0.437 µmol) and $P(o-tol)_3$ (1.1 mg, 3.61 µmol) were added, and the reaction was heated to 60 °C for 14 h. Upon full conversion of the starting material, the reaction was diluted with CH_2Cl_2 (10 mL) and washed with water (15 mL) three times. The organic phase was dried over MgSO₄, the solvent evaporated under reduced pressure, and the crude purified by column chromatography (SiO₂, gradient of hexane– CH_2Cl_2).

(38) Preparation of Compound 14

In a heat-gun-dried Schlenk tube under an atmosphere of argon, a mixture of **7** (15 mg, 21.7 µmol), iminodibenzyl (9 mg, 47.7 µmol), and Pd-RuPhos-G4 (1.8 mg, 2.17 µmol) was dissolved in dry 1,4-dioxane (0.5 mL). The resulting mixture was degassed in a stream of argon for 10 min. At this point LiHMDS (0.1 M in THF, 54 µL, 54.2 µmol) was added. After heating to 60 °C for 16 h the reaction mixture was dissolved with CH₂Cl₂ and subsequently washed with water and brine. After drying over MgSO₄ and evaporating under reduced pressure, flash column chromatography (SiO₂, hexane-CH₂Cl₂= 1:1) afforded the product as a yellow solid in 56% yield. ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.51 (dd, J = 5.4, 3.2 Hz, 8 H), 7.14 (ddd, J = 8.6, 6.5, 2.4 Hz, 12 H), 6.72 (td, J = 7.3, 1.2 Hz, 4 H), 6.54 (ddd, J = 8.7, 7.2, 1.7 Hz, 4 H), 6.37 (dd, J = 8.4, 1.2 Hz, 4 H), 5.61 (s, 4 H), 3.67 (s, 8 H) ppm. ESI-HRMS: m/z [M + H]⁺ = 921.3700; found: 921.3703.

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(39) Preparation of Compound 15

Compound 7 (20 mg, 28.9 µmol), Pd(PPh₃)₄ (6.4 mg, 5.54 µmol), and CuI (1.0 mg, 5.25 µmol) were suspended in THF-Et₃N (1:1, 1.5 mL). After degassing with argon for 15 min, TIPS acetylene (150 µL, 578 µmol) was added, and the resulting reaction mixture was stirred at 50 °C for 60 h. The green luminescent reaction mixture was quenched by addition of water (5 mL) and extracted three times with CH₂Cl₂ (10 mL). The combined organic layers were dried over MgSO₄, and the solvent was evaporated under reduced pressure. The crude was purified by column chromatography (SiO₂, hexane-CH₂Cl₂= 4:1 to 1:2). Compound 15 (15 mg, 57%) was obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₂): δ = 7.54 (dd, [3 = 5.4 Hz, [4 = 3.2 Hz, 8H, CH), 7.14 (dd, J3 = 5.4 Hz, J4 = 3.2 Hz, 8 H, CH), 5.60 (s, 4 H, CH), 1.34 (s, 36 H, CH₃), 1.26 (s, 6 H, CH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 157.7, 141.7, 140.2, 127.0, 125.4, 121.3, 107.6, 55.4, 19.1, 11.9 ppm. ESI-HRMS: m/z [M + H]⁺: 895.4586; found: 895.4566.