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Development of Thermally Activated Delayed Fluorescence Materials with Shortened Emissive Lifetimes

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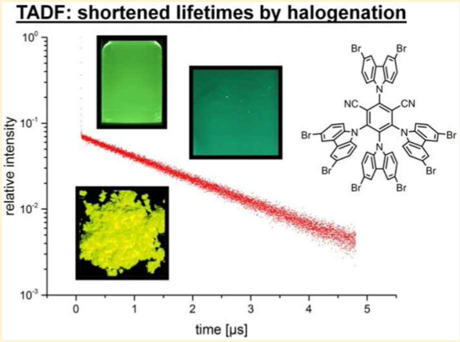
Supporting Information

ABSTRACT: We have prepared a thermally activated delayed fluorescence (TADF) capable molecular system carrying halogen substituents at the carbazole units. The attachment of the halogen atoms considerably decreases the half-life of the delayed fluorescence. The effect is significant. The heavier the halogen, the greater the effect. Our materials have the shortest reported emissive lifetimes for TADF achieved to date. Intersystem crossing (ISC) is improved through the heavy atom effect, yet high quantum yields are achieved both in solution as well as in thin doped films. The simple and efficient synthesis of our targets uses inexpensive and easily obtained starting materials.



INTRODUCTION

Here, we show that the attachment of halogen substituents to the TADF-active scaffolds **3a** (1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene) and **5a** (1,2,4,5-tetrakis(carbazol-9-yl)-3,6-dicyanobenzene) leads to compounds such as **3d** (1,2,3,5-tetrakis(3,6-dibromocarbazol-9-yl)-4,6-dicyanobenzene) and **5d** (1,2,4,5-tetrakis(3,6-dibromocarbazol-9-yl)-3,6-dicyanobenzene) with improved emissive properties, specifically, shortened emissive lifetime. In organic materials, the predominant emission mode is fluorescence, and innumerable fluorescent organic molecules have been prepared as sensors, whiteners, and colorants and also as active emitters in light-emitting diodes of different colors.[1] While fluorescence can be an efficient process, it rests upon the formation and radiative decay of singlet excitons. Optical excitation of most organic dyes leads (as opposed to inorganic or organometallic luminophors) to singlet excitons that can fluoresce with emissive lifetimes of approximately 0.1−10 ns.[2] If the excitons are formed by the combination of a hole and an electron (i.e., a radical anion and a radical cation) in the emissive layer of an organic light-emitting diode (OLED), three out of four formed excitons are triplets,[3] while only one in four is a singlet. The triplet excitons then decay by internal conversion. This effect limits the intrinsic efficiency of OLEDs, as 75% of the excitons go to waste.[4]

The harvesting of the triplet excitons is possible if triplet and excited singlet states are close in energy and reversibly interconvert. In such a scenario, excitons formed from the recombination of a hole and an electron in an organic semiconductor (i.e., in an OLED) will populate the triplet state (75%) and then interconvert slowly into the singlet state, which quickly deactivates under fluorescence; consequently, the long-lived triplet state will be harvested by conversion into the first excited singlet state, which is fluorescent. Adachi has popularized and used this concept for the fabrication of efficient OLED materials.[5] The construction principle for such materials seems to be (a) a rigid molecular frame and (b) spatial separation of the HOMO and the LUMO into a non-overlapping frontier molecular orbital structure.[6] The combination of these two design features favors a situation where singlet and triplet states are similar in energy.[7]

Molecules used by Adachi and some other groups are **3a** and **5a** and some of their derivatives.[5,8,9] The challenge in these systems is the relatively (in comparison to fluorescence lifetimes) long triplet lifetimes of 5 and 2 μs, which suggest that the time needed for the intersystem crossing, i.e. the up-conversion into the excited singlet state, is relatively slow. Shorter interconversion times would lead to faster deactivation through S_1, less time for concentration, or of other types of quenching, and therefore, a reduced degradation in OLEDs can be expected by a shorter lifetime of the excited states.

A time-honored structural concept for the acceleration of intersystem crossing (ISC) is the heavy atom effect, as the presence of a bromine or iodine substituent efficiently increases spin orbit coupling.

Our idea was to prepare the standard TADF molecules, sporting halogen substituents and investigate the change in their optical and excited state properties. We also wanted to employ an efficient synthetic approach, which could deliver the desired molecules quickly and in one step, using inexpensive, commercially available, or easily prepared starting materials. Consequently, we explored the isomeric tetrafluoroisophthalic and -terephthalic nitriles **1** and **4** as starting materials.

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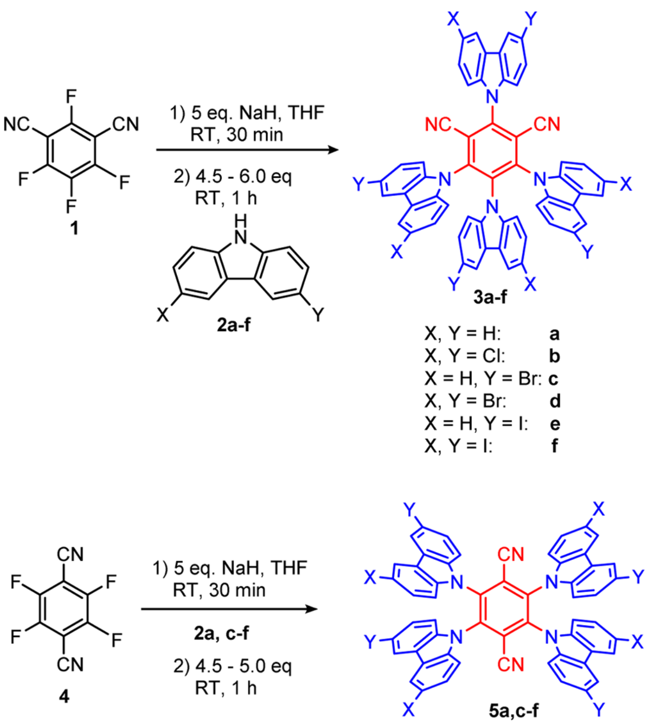
RESULTS AND DISCUSSION

Reaction of these two building blocks with the halogenated carbazoles **2a**–**f** furnishes the targets **3a**–**f** in excellent yields (Scheme 1). When **4** was used as a starting material, reaction with **2a**,**c**–**f** furnished the targets **5a**,**c**–**f** in reasonable yields as somewhat soluble, highly crystalline materials. For **3c** and **3d**, sublimation was successfully performed, allowing the use of this material in vapor deposition to build OLEDs. Simple quantum chemical calculations demonstrate that HOMO and LUMO are spatially separated, one of the apparent prerequisites for efficient TADF. Figure 1 shows the distribution of HOMO and LUMO for **3d**.

Scheme 1. Preparation of the Halogenated Derivatives 3b–f of 3a and of the Halogenated Derivatives 5c–f of 5a[a]



[a]Yields: **3a**, 65%; **3b**, 79%; **3c**, 91%; **3d**, 79%; **3e**, 67%; **3f**, 80%; **5c**, 40%; **5d**, 20%; **5e**, 73%; **5f**, 55%.

In a first experiment (Figure 2), we investigated the time-dependent emission in degassed toluene solution of both the known compound **3a** and the octabromo derivative **3d**. The emissive lifetime of **3d** is considerably shorter than that of **3a**. In addition, the share of TADF increases upon halogenations from 72% (**3a**) to almost 100%. The delayed part of the fluorescence of **3d** is much more efficient than that of **3a**; as a consequence, its intensity starts at a much higher value.

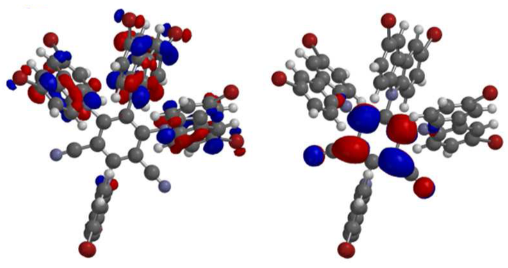


Figure 1. HOMO (left) and LUMO (right) of **3d** for S_0 according to the DFT calculations of S_0 using the optimized geometry.

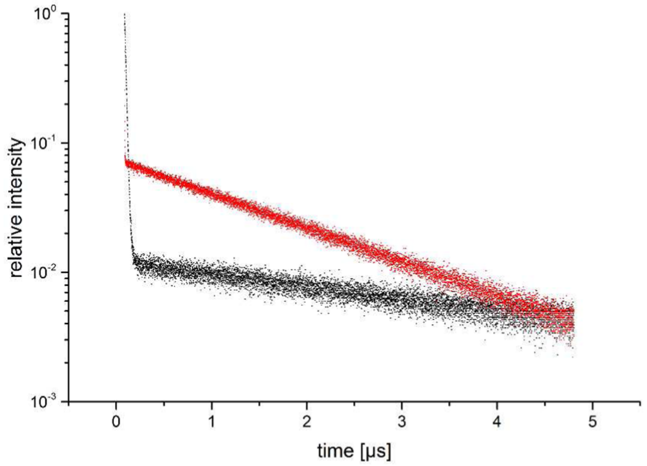


Figure 2. Time-dependent fluorescence of **3a** (black dots) and **3d** (red dots) in degassed toluene solution at room temperature.

This experiment demonstrates that (a) TADF is possible with brominated Adachi-type chromophores such as **3d** and that (b) halogenation increases the rate of (reverse) ISC and therefore the population of the S_1 state due to the heavy atom effect. We have also looked at the photophysical properties of other halogenated derivatives of **3a** and **5a**. Interestingly, increasing the degree of bromination does not seem to change the absorption and emission wavelengths significantly (Figure 3) when going from **3a** via **3c** to **3d**.

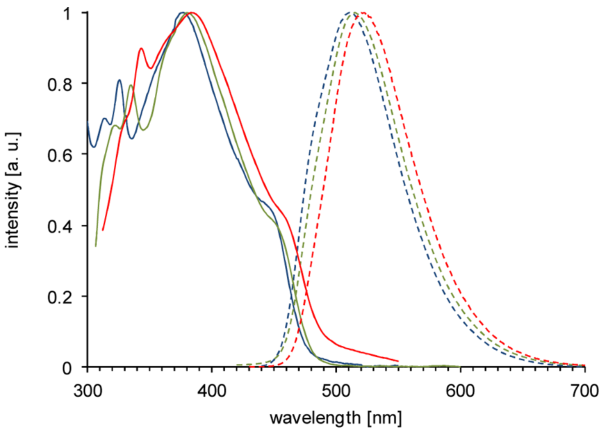


Figure 3. Absorption (solid lines) and emission (dashed lines) spectra of **3a** (blue), **3c** (green), and **3d** (red) in toluene at room temperature.

Table 1 shows the photophysical data of **3a**–**f** and of **5a**,**c**–**f**. It is noteworthy that the quantum yield of **3a**–**c** is only slightly reduced upon addition of the bromine substituent in toluene; upon octabromination (**3d**), the quantum yield in toluene drops from 0.88 to 0.67. Both the reduced quantum yields as well as decreased lifetimes in air-equilibrated solution prove the substances to be TADF materials, as the triplet excitons are quenched by oxygen. To investigate further, we determined the quantum yields of several halogenated derivatives in poly(methyl methacrylate) (PMMA) films (Table 1). Generally, the quantum yields in PMMA films are *higher* than the quantum yields in toluene. The reason is the rigidification of the molecular framework the molecules experience through the

Table 1. Photophysical Data of 3a–f and 5a,c–f

	λ_{abs} in degassed toluene (nm)	λ_{em} in degassed toluene (nm)	OY in degassed toluene (%)	QY in air-equilibrated toluene (%)	QY in PMMA film (%)	rel portion of delayed fluorescence in degassed toluene (%)	fluorescence lifetime in degassed toluene (μs)	fluorescence lifetime in air-equilibrated toluene (μs)	fluorescence lifetime in PMMA film (μs)
3a	375	507	88[a]	25	9	72	5.1	0.4	5.3
3b	384	518	76	24	88	83	2.3	0.4	2.6
3c	381	515	85	15	95	98	2.2	0.4	2.5
3d	374	521	67	20	86	97	1.6	0.4	2.0
3e	383	518	78	15	93	97	1.9	0.4	2.2
3f	384	533	70	22	[b]	99	1.2	0.4	[b]
5a		535 (lit.)	72 (lit.)				1.9 (lit.)		
5c	337	543	53	25	64	92	1.2	0.4	1.4
5d	339	546	45	27	[b]	95	0.8	0.4	[b]
5e	348	548	45	20	66	98	0.8	0.3	1.0
5f	361	562	27	18	[b]	96	0.4	0.1	[b]

[a] QY of 94% in literature.[5] [b] Due to low solubility, films could not be obtained for this substance.

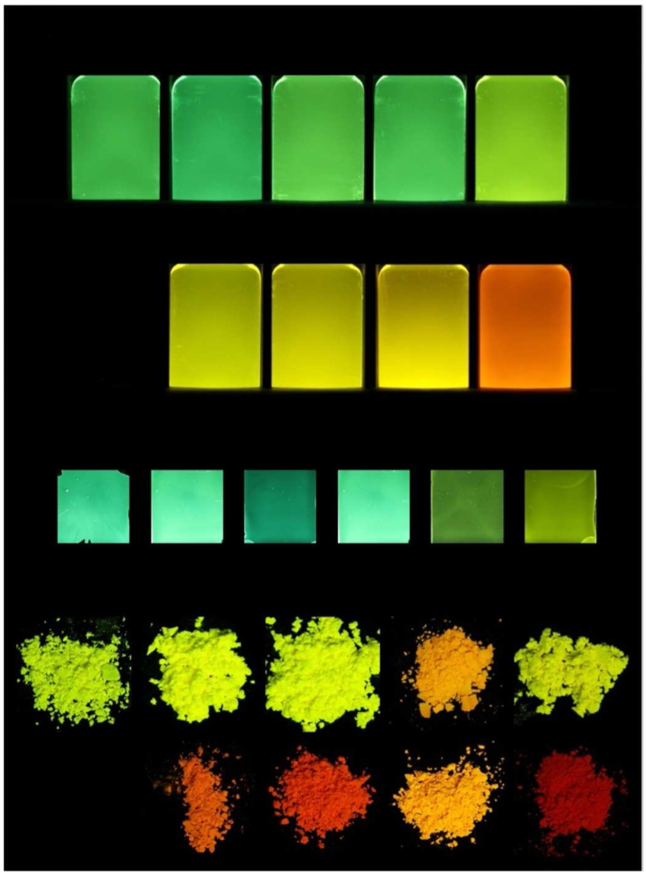


Figure 4. First row: fluorescence of **3b**–**f** in toluene. Second row: fluorescence of **5c**–**f** in toluene. Third row: fluorescence of **3b**–**e**, **5c**, and **5e** in films (5 wt % in PMMA). Fourth row: fluorescence of the solid materials **3b**–**f**. Fifth row: fluorescence of the solid materials **5c**–**f**. All irradiated at 365 nm.

Table 2. Measured and Calculated Energy Gaps of 3a,c,d and 5e

	S_0S_1 gap[a] (eV)	S_0T_1 gap[b] (eV)	S_1T_1 gap[c] (eV)
3a	2.64	2.59	0.05
3c	2.63	2.59	0.04
3d	2.61	2.57	0.04
5e	2.38	2.34	0.04

[a] Determined from the onset of the absorption in 2-methyltetrahydrofuran. [b] Determined from the maximum of emission at 77 K in 2-methyltetrahydrofuran. [c] Calculated from the difference between S_0T_1 gap and S_0S_1 gap.

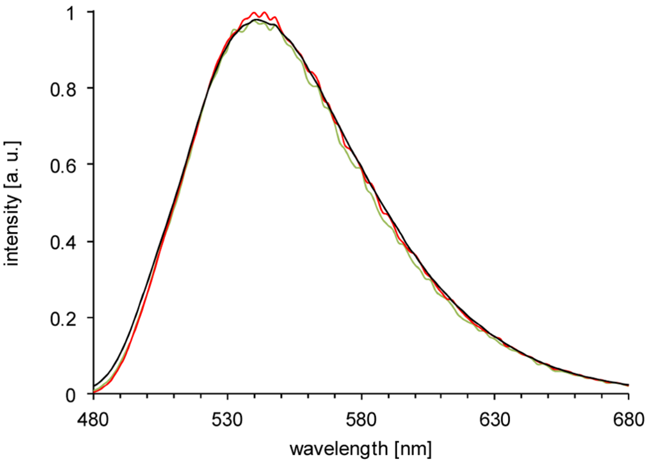


Figure 5. Emission spectra of **3d**: direct fluorescence (black line), 50 ns delay (green line), and 1000 ns delay (red line).

embedding instilled by the polymeric matrix. These experiments mimic emission of such TADF in matrix materials and suggest that they will be useful in OLEDs.

Table 2 shows the triplet energies obtained from low-temperature measurements in 2-methyltetrahydrofuran at 77 K of **3a**, **3c**, **3d**, and **5e**, which prove the small singlet–triplet gap. Photographs of the fluorescence of **3b**–**f** and **5c**–**f** in the solid state, solution, and film are shown in Figure 4. In Figure 5, the emission spectra of **3d** of the direct fluorescence (0 ns delay) and of the delayed fluorescence (50 and 1000 ns delay) are displayed. The similarity proves that both direct and delayed emission spectra come from identical states.

The most important issue of this study is the influence of the halogen substituents on the excited state lifetime (here in toluene). Table 1 and Figure 5 are instructive and demonstrate the power of four or eight halogen substituents. While **3f** and **5f** carrying eight iodine substituents have the shortest emissive lifetimes with 1.2 and 0.4 μs, respectively, their quantum yields are also the lowest, and due to their poor solubility, neither of the two derivatives could be processed into PMMA films. As a consequence, octabrominated **3d** and tetraiodinated **5e** with 1.6 and 0.8 μs excited state lifetimes are the two most exciting

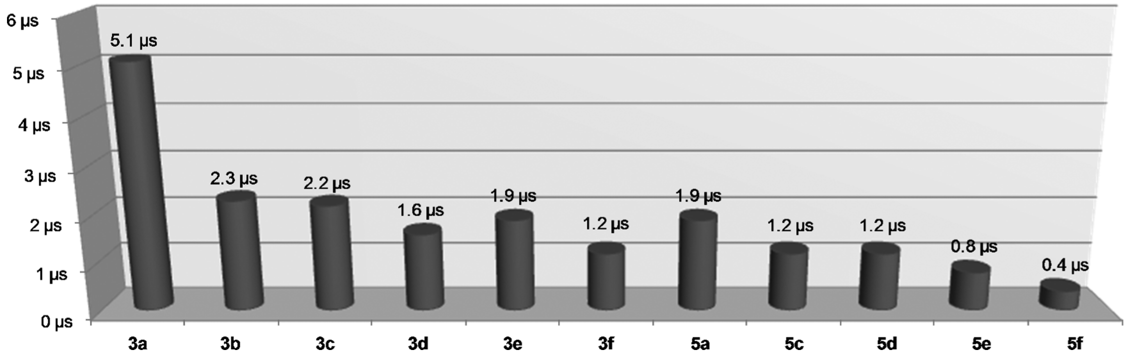


Figure 6. Fluorescence lifetimes of **3a**−**f** and **5a**,**c**−**f** in toluene solution.

derivatives that show significant potential in further applications. For **3d**, the lifetime is reduced to 31% of that of **3a**, while for **5e** the lifetime is reduced to 42% when compared to that of **5a** (Figure 6).

In conclusion, the addition of halogen atoms as substituents into Adachi-type TADF-emitters[5] leads to a significant shortening of the excited state lifetimes. The halogen substituents work as singlet−triplet interconverters through the heavy atom effect, facilitating intersystem crossing. At the same time, while being effective at intersystem crossing, the halogen atoms only slightly decrease the emission quantum yields. Therefore, the halogenation will make these compounds supremely useful in future applications in OLEDs.

■ EXPERIMENTAL SECTION

All reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise noted. Preparation of air- and moisture-sensitive materials was carried out in flame-dried flasks under an atmosphere of nitrogen by using Schlenk techniques. Thin layer chromatograms were obtained using polygram-TLC-plates. Column chromatography was performed using standard grade silica gel 60 Å 32−63 μm (230 × 450 mesh).

Gel permeation chromatography was performed using polystyrene polymers. ^{1}H and ^{13}C spectra were recorded at 298 K on a 300, 400, or 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$, acetone-d_5, or dimethyl-d_5 sulfoxide in the corresponding deuterated solvent. Coupling constants (J) are reported in hertz. Infrared (IR) spectra are reported in wavenumbers (cm^{-1}). DFT calculations were carried out using Spartan 10 version 1.1.0 with 6-31G as basis set. Films were obtained by spin-coating with a solution of 47.5 mg/mL of PMMA and 2.5 mg/mL of the emitter in chlorobenzene with a rotation of 500 rpm for 30 s followed by 3000 rpm for 10 s. All measurements were obtained at room temperature; all solutions were degassed by bubbling nitrogen through for 10 min before measuring unless otherwise noted. Concentrations of all solutions were set so that the absorption maximum was below 0.1. Low-temperature measurements were performed by cooling a solution of the material in 2-methyltetrahydrofuran to 77 K and recording the luminescence. Fluorescence lifetimes and delayed emission spectra were determined using a pulsed light source (excitation wavelength: 376 nm, pulse duration: < 200 ns). Photoluminescent quantum yields were determined using an emission spectrometer equipped with an integration sphere. The system was calibrated with a primary light source. The procedure from Würth et al. was used.[11]

3-Iodocarbazole (**2e**), 3,6-diiodocarbazole (**2f**), and 2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyanobenzene (**3a**) were prepared according to the literature.[5,10]

3-Iodocarbazole 2e. Carbazole (5.00 g, 29.9 mmol, 1.00 equiv) and potassium iodide (2.98 g, 17.9 mmol, 0.60 equiv) were suspended in acetic acid (75 mL) and heated to 80 °C. Then potassium iodate (3.84 g, 17.9 mmol, 0.60 equiv) was added. After a few minutes, the violet color indicated the formation of iodine. The mixture was stirred at 80 °C for 1 h. The consumption of carbazole was checked by UHPLC−MS, and then the reaction mixture was poured into water (100 mL) and the precipitate was filtered off. The residue was washed with a saturated aqueous sodium sulfite solution (200 mL) first and then with water (200 mL). The crude product was recrystallized from toluene two times to yield a colorless solid (1.28 g, 15%). ^{1}H NMR (acetone-d_6, 300 MHz, δ): 10.48 (s, 1 H), 8.49 (d, J = 1.7 Hz, 1 H), 8.15 (d, J = 7.8 Hz, 1 H), 7.67 (dd, J = 8.5, 1.7 Hz,1 H), 7.53 (d, J = 8.2 Hz, 1 H), 7.45−7.38 (m, 2 H), 7.21 (td, J = 7.5, 1.0 Hz,1 H). Spectral data were in agreement with the literature.[10]

3,6-Diiodocarbazole 2f. Prepared according to the literature: Carbazole (3.00 g, 17.9 mmol, 1.00 equiv) and potassium iodide (3.57 g, 21.5 mmol, 1.20 equiv) were suspended in acetic acid (30 mL) and heated to 80 °C. Then potassium iodate (4.61 g, 21.5 mmol, 1.20 equiv) was added. After a few minutes, the violet color indicated the formation of iodine. The mixture was stirred at 80 °C for 1.5 h. The consumption of carbazole was checked by UHPLC−MS. The reaction mixture was poured into water (100 mL), and the precipitate was filtered off. This was washed with a saturated aqueous solution of sodium sulfite (200 mL) first and then with water (200 mL). The crude product was recrystallized from toluene two times to give a total yield 4.10 g (55%) of a colorless solid: ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 8.32 (d, J = 1.6 Hz, 2 H), 8.17 (s, 1 H), 7.68 (dd, J = 8.5, 1.6 Hz, 2 H), 7.21 (dd, J = 8.5 Hz, J = 1.6 Hz, 2 H). Spectral data were in agreement with the literature.[10]

GP for the Synthesis of Tetracarbazoledicyanobenzenes 3a−f, 5a,c−f. Under a nitrogen atmosphere, carbazole (4.50−6.00 equiv) was dissolved in dry THF (2 mL). Sodium hydride (5.00−8.00 equiv) was added, and the suspension was stirred at room temperature for 30 min. After 2,4,5,6-tetrafluoro-1,3-dicyanobenzene (1.00 equiv) or 2,3,5,6-tetrafluoro-1,4-dicyanobenzene (1.00 equiv), respectively, had been added, stirring was continued for 1 h. Completion of the reaction was checked by UHPLC−MS. The reaction mixture was quenched with water (2 mL).

2,4,5,6-Tetrakis(carbazol-9-yl)-1,3-dicyanobenzene 3a. Prepared according to the general procedure from carbazole (418 mg, 2.50 mmol, 5.00 equiv), sodium hydride (72.0 mg, 3.00 mmol, 6.00 equiv), and 2,4,5,6 tetrafluoro-1,3-dicyanobenzene (100 mg, 500 μmol, 1.00 equiv) in dry THF (2 mL). Purification was performed by GPC (THF) and then by filtration through a short silica column (DCM) to yield a yellow solid (256 mg, 65%): ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 8.22 (d, J = 7.7 Hz, 2 H), 7.72−7.67 (m, 8 H), 7.50−7.49 (t, J = 7.4 Hz, 2 H), 7.33 (d, J = 7.4 Hz, 2 H), 7.22 (d, J = 7.7 Hz, 4 H), 7.11−7.05 (m, 8 H), 6.82 (t, J = 7.7 Hz, 4 H), 6.63 (t, J = 7.7 Hz, 2 H). Spectral data were in agreement with the literature.[5]

2,4,5,6-Tetrakis(3,6-dichlorocarbazol-9-yl)-1,3-dicyanobenzene 3b. Prepared according to the general procedure from 3,6-dichlorocarbazole (147 mg, 625 μmol, 5.00 equiv), sodium hydride (24.0 mg, 1.00 mmol, 8.00 equiv), and 2,4,5,6 tetrafluoro-1,3-dicyanobenzene (25.0 mg, 125 μmol, 1.00 equiv) in dry THF (1 mL). Purification was performed by GPC (THF) and then by filtration through a short silica column (DCM) to yield a yellow solid (105 mg, 79%): ^{1}H NMR ($CDCl_3$, 400 MHz, δ) 8.16 (s, 2 H), 7.73 (s, 4 H), 7.68 (d, *J* = 8.7 Hz, 2 H), 7.48 (m, 2 H), 7.42 (s, 2 H), 7.14 (d, *J* = 8.7 Hz, 4 H), 7.02 (t, *J* = 8.7 Hz, 4 H), 6.74 (d, *J* = 8.7 Hz, 2 H), 6.66 (d, *J* = 8.7 Hz, 2 H); due to the poor solubility it was not possible to obtain a ^{13}C NMR spectrum; IR (cm^{-1}) 1544, 1464, 1430, 1297, 1278, 1217, 1080, 1024, 856, 799, 693, 560, 522, 423; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{24}Cl_8N_6$, calcd 1059.95762, found 1059.95698. Anal. Calcd for $C_{56}H_{24}Cl_8N_6$: C, 63.19; H, 2.27; N, 7.90; Cl, 26.64. Found: C, 62.93; H, 2.55; N, 7.66; Cl, 26.48.

2,4,5,6-Tetrakis(3-bromocarbazol-9-yl)-1,3-dicyanobenzene 3c. Prepared according to the general procedure from 3-bromocarbazole (123 mg, 500 μmol, 5.00 equiv), sodium hydride (17.0 mg, 700 μmol, 7.00 equiv), and 2,4,5,6 tetrafluoro-1,3-dicyanobenzene (20.0 mg, 100 μmol, 1.00 equiv) in dry THF (2 mL). Purification was performed by GPC (THF) and then by filtration through a short silica column (DCM) to yield a yellow solid (100 mg, 91%): ^{1}H NMR (DMSO-d_6, 400 MHz, δ) 8.65 (s, 1 H), 8.42 (d, *J* = 7.7 Hz, 1 H),8.21−8.18 (m, 2 H), 8.14−8.11 (m, 2 H), 7.96−7.93 (m, 3 H), 7.84−7.78 (m, 3 H), 7.73−7.67 (m, 2 H), 7.61−7.56 (m, 2 H), 7.54−7.30 (m, 5 H), 7.26−7.09 (m, 4 H), 6.97−6.74 (m, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz, δ) 145.2, 144.7, 140.0, 138.8, 138.8, 138.7, 138. 6, 138.5, 137.9, 137.8, 137.4, 137.3, 136.4, 136.1, 129.3, 128.1, 128.0, 127.9, 127.8, 127.7, 126.6, 126.4, 126.3, 126.2, 125.7, 125.3, 125.3, 125.2, 124.9, 123.8, 123.1, 122.6, 122.4, 122.2, 121.8, 121.7, 121.2, 120.9, 120.2, 116.8, 114.5, 113.8, 113.7, 113.7, 112.9, 112.9, 112.8, 112.7, 112.6, 112.5, 111.9, 111.1, 111.1, 111.0, 110.9, 110.8; IR (cm^{-1}) 1438, 1324, 1297, 1267, 1217, 1058, 1027, 799, 742, 552, 419; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{28}{}^{79}Br_2{}^{81}Br_2N_6$, calcd 1103.90735, found 1103.90620. Anal. Calcd for $C_{56}H_{28}Br_4N_6$: C, 60.90; H, 2.56; N, 7.61; Br, 28.94. Found: C, 61.10; H, 2.71; N, 7.68; Br, 29.13.

2,4,5,6-Tetrakis(3,6-dibromocarbazol-9-yl)-1,3-dicyanobenzene 3d. Prepared according to the general procedure from 3,6-dibromocarbazole (9.50 g, 29.2 mmol, 4.50 equiv), sodium hydride (1.09 g, 45.5 mmol, 7.00 equiv), and 2,4,5,6 tetrafluoro-1,3-dicyanobenzene (1.30 mg, 6.50 mmol, 1.00 equiv) in dry THF (60 mL). Purification was performed by recrystallization from acetone to yield a yellow solid (7.28 g, 79%): ^{1}H NMR (DMSO-d_6, 400 MHz, δ) 8.73 (m, 2 H), 8.29 (d, 4 H), 8.04−7.94 (m, 6 H), 7.65 (d, *J* = 8.8 Hz, 4 H), 7.44−7.41 (m, 6 H), 7.04 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz, δ) 145.0, 144.5, 138.6, 137.6, 136.7, 135.9, 130.3, 129.0, 127.8, 124.6, 124.5, 124.2, 123.8, 123.7, 123.2, 116.8, 114.8, 114.3, 113.5, 112.9, 112.6, 111.5; IR (cm^{-1}) 3069, 1540, 1464, 1427, 1297, 1274, 1217, 1062, 1020, 826, 795, 634, 556, 487, 419; HR-MS (MALDI pos, *m/z*) M$^+$ = $C_{56}H_{24}{}^{79}Br_4{}^{81}Br_4N_6$, calcd 1419.54421, found 1419.55640. Anal. Calcd for $C_{56}H_{24}Br_8N_6$: C, 47.36; H, 1.70; N, 5.92; Br, 45.01. Found: C, 47.11; H, 1.82; N, 6.06; Br, 44.92.

2,4,5,6-Tetrakis(3-iodocarbazol-9-yl)-1,3-dicyanobenzene 3e. Prepared according to the general procedure from 3-iodocarbazole 132 mg, 450 μmol, 4.50 equiv), sodium hydride (17.0 mg, 700 μmol, 7.00 equiv), and 2,4,5,6 tetrafluoro-1,3-dicyanobenzene (20.0 mg, 100 μmol, 1.00 equiv) in dry THF (2 mL). Purification was performed by GPC (THF) and then by filtration through a short silica column (DCM) to yield a yellow solid (87.0 mg, 67%): ^{1}H NMR (DMSO-d_6, 400 MHz, δ) 8.78 (s, 1 H), 8.40 (d, *J* = 7.8 Hz, 1 H),8.34−8.32 (m, 2 H), 8.10−8.06 (m, 2 H), 8.00−7.91 (m, 4 H), 7.78 (t, *J* = 7.6 Hz, 1 H), 7.72−7.67 (m, 2 H), 7.63−7.44 (m, 7 H), 7.38 (t, *J* = 7.1 Hz, 1 H), 7.24−6.98 (m, 5 H), 6.92−675 (m, 2 H); ^{13}C NMR (DMSO-d_6, 100 MHz, δ) 145.3, 145.2, 144.6, 139.7, 139.0, 138.6, 138.5, 138.4, 138.3, 138.0, 137.8, 137.7, 137.6, 137.0, 136.1, 134.8, 133.6, 133.4, 132.2, 132.1, 129.7, 128.9, 128.3, 127.6, 126.3, 126.2, 126.0, 125.8, 125.4, 125.4, 125.1, 122.4, 122.3, 122.0, 121.9, 121.6, 121.5, 121.2, 120.8, 120.1, 116.7, 113.3, 113.2, 113.0, 111.9, 112.0, 110.9, 85.8, 85.1, 84.2; IR (cm^{-1}) 1434, 1316, 1217, 1027, 792, 742, 571, 552, 423; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{28}I_4N_6$, calcd 1291.85597, found 1291.85535. Anal. Calcd for $C_{56}H_{28}I_4N_6$: C, 52.04; H, 2.18; N, 6.50. Found: C, 51.87; H, 2.37; N, 6.44.

2,4,5,6-Tetrakis(3,6-diiodocarbazol-9-yl)-1,3-dicyanobenzene 3f. Prepared according to the general procedure from 3,6-diiodocarbazole (251 mg, 600 μmol, 6.00 equiv), sodium hydride (19.0 mg, 800 μmol, 8.00 equiv), and 2,4,5,6 tetrafluoro-1,3-dicyanobenzene (20.0 mg, 100 μmol, 1.00 equiv) in dry THF (2 mL). Purification was performed by recrystallization from toluene first and then from acetone to yield a yellow solid (158 mg, 80%): ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 8.85 (s, 2 H), 8.42 (s, 4 H), 8.10 (d, *J* = 8.5 Hz, 2 H), 8.06 (s, 2 H), 7.87 (d, *J* = 8.5 Hz, 2 H), 7.55−7.49 (m, 8 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.15 (d, *J* = 7.9 Hz, 2 H); due to the poor solubility it was not possible to obtain a ^{13}C NMR spectrum; IR (cm^{-1}) 3061, 1700, 1540, 1461, 1419, 1278, 1213, 1050, 1020, 868, 788, 632, 552, 476; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{24}I_8N_6$, calcd 1795.44254, found 1795.44319. Anal. Calcd for $C_{56}H_{24}I_8N_6$: C, 37.45; H, 1.35; N, 4.68. Found: C, 37.44; H, 1.46; N, 4.72.

2,3,5,6-Tetrakis(3-bromocarbazol-9-yl)-1,4-dicyanobenzene 5c. Prepared according to the general procedure from 3-bromocarbazole (72.0 mg, 292 μmol, 4.50 equiv), sodium hydride (7.80 mg, 320 μmol, 5.00 equiv), and 2,3,5,6 tetrafluoro-1,4-dicyanobenzene (13.0 mg, 65.0 μmol, 1.00 equiv) in dry THF (1 mL). Purification was performed by GPC (THF) and then by refluxing the crude product in methanol (10 mL) for 10 min and filtering off the residue to yield an orange solid (29.0 mg, 40%): ^{1}H NMR (DMSO-d_6, 400 MHz, δ) 8.25−8.22 (m, 4 H), 8.21−7.98 (m, 4 H), 7.95−7.72 (m, 8 H), 7.55−7.45 (m, 3 H), 7.43−7.40 (m, 1 H), 7.38−7.28 (m, 3 H), 7.26−7.16 (m, 5 H); due to the poor solubility it was not possible to obtain a ^{13}C NMR spectrum; IR (cm^{-1}) 1616, 1434, 1320, 1267, 1214, 1058, 1027, 784, 735, 575, 553, 461; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{28}{}^{79}Br_2{}^{81}Br_2N_6$, calcd 1103.90680, found 1103.90762. Anal. Calcd for $C_{56}H_{28}Br_4N_6$: C, 60.90; H, 2.56; N, 7.61; Br, 28.94. Found: C, 60.68; H, 2.70; N, 7.82; Br, 28.89.

2,3,5,6-Tetrakis(3,6-dibromocarbazol-9-yl)-1,4-dicyanobenzene 5d. Prepared according to the general procedure from 3,6-dibromocarbazole (365 mg, 1.12 mmol, 4.50 equiv), sodium hydride (30.0 mg, 1.25 mmol, 5.00 equiv), and 2,3,5,6 tetrafluoro-1,4-dicyanobenzene (50.0 mg, 250 μmol, 1.00 equiv) in dry THF (4 mL). Purification was performed by refluxing the crude product in acetone (10 mL) for 10 min and filtering off the residue to yield an orange solid (70.0 mg, 20%): ^{1}H NMR (DMSO-d_6, 500 MHz, δ) 8.35 (d, *J* = 1.8 Hz, 8 H), 7.74 (d, *J* = 8.7 Hz, 8 H), 7.52 (dd, *J* = 8.7, 1.8 Hz, 8 H); due to the poor solubility it was not possible to obtain a ^{13}C NMR spectrum; IR (cm^{-1}) 1465, 1426, 1279, 1225, 1058, 1027, 825, 795, 643, 559, 488, 416; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{24}{}^{79}Br_4{}^{81}Br_4N_6$, calcd 1419.54531, found 1419.54463. Anal. Calcd for $C_{56}H_{24}Br_8N_6$: C, 47.36; H, 1.70; N, 5.92; Br, 45.01. Found: C, 47.33; H, 1.79; N, 5.69; Br, 45.18.

2,3,5,6-Tetrakis(3-iodocarbazol-9-yl)-1,4-dicyanobenzene 5e. Prepared according to the general procedure from 3-iodocarbazole (165 mg, 562 μmol, 4.50 equiv), sodium hydride (15.0 mg, 625 μmol, 5.00 equiv), and 2,3,5,6 tetrafluoro-1,4-dicyanobenzene (25.0 mg, 125 μmol, 1.00 equiv) in dry THF (1 mL). Purification was performed by GPC (THF) and then by refluxing the crude product in methanol (10 mL) for 10 min and filtering off the residue to yield an orange solid (117 mg, 73%): ^{1}H NMR (DMSO-d_6, 400 MHz, δ) 8.39−8.37 (m, 4 H), 8.00−7.97 (m, 4 H), 7.97−7.54 (m, 12 H), 7.35−7.16 (m, 8 H); due to the poor solubility it was not possible to obtain a ^{13}C NMR spectrum; IR (cm^{-1}) 1666, 1616, 1487, 1449, 1362, 1320, 1275, 1217, 1152, 1027, 876, 788, 735, 575, 553, 457; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{28}I_4N_6$, calcd 1291.85542, found 1291.85438. Anal. Calcd for $C_{56}H_{28}I_4N_6$: C, 52.04; H, 2.18; N, 6.50. Found: C, 51.96; H, 2.43; N, 6.52.

2,3,5,6-Tetrakis(3,6-diiodocarbazol-9-yl)-1,4-dicyanobenzene 5f. Prepared according to the general procedure from 3,6-diiodocarbazole (471 mg, 1.12 mmol, 4.50 equiv), sodium hydride (30.0 mg, 1.25 mmol, 5.00 equiv), and 2,3,5,6 tetrafluoro-1,4-dicyanobenzene (50.0 mg, 250 μmol, 1.00 equiv) in dry THF (4 mL). Purification was performed by refluxing the crude product in acetone (10 mL) for 10 min and filtering off the residue to yield an orange solid (245.0 mg, 55%): ^{1}H NMR (DMSO-d_6, 500 MHz, δ) 8.48 (m, 8 H), 7.64 (m, 16 H); due to the poor solubility it was not possible to obtain a ^{13}C NMR spectrum; IR (cm^{-1}) 1704, 1491, 1469, 1422, 1279, 1217, 1019, 864, 795, 628, 555, 472, 412; HR-MS (MALDI neg, *m/z*) M$^-$ = $C_{56}H_{24}I_8N_6$, calcd 1795.44254, found

1795.44061. Anal. Calcd for $C_{56}H_{24}I_8N_6$: C, 37.45; H, 1.35; N, 4.68. Found: C, 37.45; H, 1.44; N, 4.57.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01496.

> Figures giving time-dependent fluorescence, absorption, and emission spectra of **3a−f** and **5c−f**, ^{1}H and ^{13}C NMR spectra of **3b−f** and **5c−f**, as well as tables giving the Cartesian coordinates of computational data for **3d** (PDF)

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Notes

The authors declare no competing financial interest.

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