Organic thermally activated delayed fluorescence material with strained benzoguanididine donor

Alexander C. Brannan¹, Elvie F. P. Beaumont¹, Nguyen Le Phuoc², George F. S. Whitehead¹, Mikko Linnolahti*² and Alexander S. Romanov*¹

Abstract
Organic thermally activated delayed fluorescence (TADF) materials have been widely investigated due to their impressive electronic properties and applied potential for the third generation of organic light-emitting diodes (OLED). We present organic TADF material (4BGIPN) based on the strained benzoguanididine donor and compare it with the benchmark carbazole-based material (4CzIPN). Extended π-conjugation in 4BGIPN material results in yellow-green luminescence at 512 nm with a fast radiative rate of 5.5 × 10⁻⁵ s⁻¹ and a photoluminescence quantum yield of 46% in methylcyclohexane solution. Such a nitrogen-rich 4BGIPN material has a significantly stabilized highest occupied molecular orbital (HOMO) at −6.4 eV while the lowest unoccupied molecular orbital (LUMO) at −4.0 eV, indicating potential suitability for application as the electron transport layer or TADF class III emitter in OLEDs.

Introduction
Thermally activated delayed fluorescence (TADF) is a photoluminescence mechanism where excitons undergo thermally-assisted reverse-intersystem crossing from an excited triplet state to a higher-lying in energy singlet state to emit delayed fluorescence [1-3]. Organic TADF emitters have gained substantial attention in recent years for their prospective application in organic light-emitting diodes (OLEDs), photocatalysis, bioimaging, and sensors [4-6]. The ability to harvest both singlet and triplet excitons enable organic TADF emitters to compete with classic phosphorescent emitters that employ scarce metals such as iridium and platinum [7-9]. Since its first report in 2012 by Uoyama et al., 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) has been a benchmark TADF emitter due to its high quantum yields and excellent performance in OLED devices [1]. 4CzIPN is a donor-acceptor-type system where carbazole donor ligands are bound to the benzo-
nitrile acceptor core moiety. In this work we have substituted the carbazole donors with 5H-benzo[\(d\)]benzo[4,5]imidazo[1,2-\(a\)]imidazole (benzoguanidine) ligands to give 4BGIPN, see Figure 1. Benzoguanidine has an extended \(\pi\)-conjugation compared with carbazole and is more nitrogen-rich (three N-atoms vs one in carbazole). Thompson et al. recently reported a series of carbene–metal–amide (CMA) (metal = Cu, Ag, Au) emitters employing a benzoguanidine ligand [10]. The extended \(\pi\)-conjugation of benzoguanidine induced a larger hole–electron separation resulting in a smaller energy gap between the excited singlet and triplet states (\(S_1\) and \(T_1\)) and \(\Delta E_{ST}\) resulting in faster radiative rates. This study aimed to synthesize and explore the luminescent properties of the 4BGIPN material containing a rigid benzoguanidine ligand in its molecular structure.

**Results and Discussion**

**Synthesis and structure**

4BGIPN was prepared in 70% yield by aromatic nucleophilic substitution reaction from 2,4,5,6-tetrafluoroisophthalonitrile and 5H-benzo[\(d\)]benzo[4,5]imidazo[1,2-\(a\)]imidazole (benzoguanidine) after deprotonation the latter with sodium hydride base. The compound shows poor solubility in most common organic solvents with moderate solubility in dichloromethane, 1,2-dichlorobenzene and dimethyl sulfoxide (DMSO). Compound 4BGIPN was characterized by high-resolution mass spectrometry (HRMS), elemental analysis, and \(^1\)H/\(^{13}\)C NMR spectroscopy. Proton NMR shows a complicated set of overlapping multiplets indicating that the reaction results in the formation of various isomers (rotamers) which are different by relative orientation of the benzoguanidine donor moieties with respect to each other (Figure 2, see Supporting Information File 1 for NMR). In DMSO-\(d_6\) solution, 4BGIPN isomers do not show interconversion even upon warming to 120 °C, resulting in a similar set of signals. Excellent fit between HRMS and elemental analysis further supports the formation of the isomeric mixture of 4BGIPN as evidenced by the identical molecular peak ion and C, H, N values within acceptable deviation of 0.4%. The decomposition temperature (\(T_d\), corresponds to 5% weight loss) was measured by thermogravimetric analysis (TGA) indicating excellent thermal stability for 4BGIPN with \(T_d = 425 \, ^\circ\)C, which is similar to the benchmark material 4CzIPN, having a \(T_d\) in the range of 402–449 °C (\(T_d\) range is dependent on the type of the 4CzIPN polymorph) [11,12]. Differential scanning calorimetry (DSC) shows an endothermic process in the range of 237 to 265 °C which can be associated with the glass transition temperature (\(T_g\)) for the isomeric mixture of 4BGIPN. This is expectedly higher than the analogous \(T_g\) of 176 °C for the 4CzIPN material [13] due to a lower molecular mass of the latter (Figure S1, Supporting Information File 1).

Single crystals for X-ray diffraction study were obtained by slow layer diffusion of hexanes into dichloromethane solution for 4BGIPN at room temperature (Figure 2). The title compound crystallizes with two independent molecules in the unit cell of the triclinic (\(P\)-1, Figure 2c, yellow plates) and monoclinic chiral space group \(P2_1\) (Figure 2a,b,d, yellow blocks). Due to very weak reflection data, the structure of 4BGIPN in triclinic form was refined in isotropic model, therefore, we do not discuss in detail the structural parameters. We only note that both forms are not due to the polymorphism but rather due to rotational isomerism of the 4BGIPN material, i.e., different orientation of the benzoguanidine donor ligands above or below the central 4,6-dicyanobenzene ring. In the monoclinic form the two independent molecules of 4BGIPN are related by a pseudo glide plane that do not completely align when superimposed through a glide operation. There is no evidence for systematic absences relating to the presence of a glide plane in the data.
Figure 2: Crystal structure for compound 4BGIPN in monoclinic form ((a) top view and (b) side view) where black arrows show opposite orientation of the benzoguanidine moieties around the central benzene ring. Representative example for the torsion angle $\alpha$ is shown in red; (c) Crystal structure for compound 4BGIPN in triclinic form; (d) packing diagram with key geometrical parameters and intermolecular contacts shown as a cyan dashed line; (e) possible isomers for 4BGIPN material. Ellipsoids are shown at the 50% level where hydrogen atoms are omitted for clarity.

supporting the refinement in the chiral $P_{2_1}$ space group. The structure was refined as a two-component inversion twin; the crystal structure as a whole is a racemic mixture of both orientations. The $C_{benzene}-N_{benzoguanidine}$ bond length varies within the error of the experiment from 1.402(5) to 1.420(5), giving an average of 1.407(13) Å for 4BGIPN, which is closely similar to 1.405(8) Å reported for the benchmark 4CZIPN compound.

Unlike carbazole, the benzoguanidine ligand lacks $C_2$ rotational symmetry, thus enabling the benzoguanidine ligands to project above and below the plane of the central benzene ring. In both molecules in the asymmetric unit, the benzoguanidine moieties bound to the benzene carbon neighboring two nitrile groups, is orientated in the opposing projection about the plane of the benzene ring to the remaining benzoguanidine moieties (Figure 2b). Unlike monoclinic, the triclinic form of 4BGIPN possesses two donor moieties pointing down at C1 and C3 carbon atoms while donor moieties at C2 and C5 are pointed up (Figure 2c). Several possible 4BGIPN rotational isomers are demonstrated in Figure 2e, however, not isolated in this work.

Compound 4BGIPN possesses a twisted orientation between the donor (benzoguanidine) and acceptor (benzonitrile) ligands (Figure 2) due to steric hindrance imposed by benzoguanidine ligands and reflected by the torsion angle ($\alpha$) laying in the range of 42.5(2)–64.3(2)$^\circ$. We compared it with the more narrow torsion angle range of 55.1(2)–60.2(2)$^\circ$ for 4CzIPN thus indicating that various carbazole donor ligands possess a very similar twist orientation [12]. The donor–acceptor twist angle has been demonstrated to be one of the key structural parameters enabling fast radiative rates for purely organic TADF materials since it’s directly related with the overlap integral between HOMO and LUMO orbitals and influences the energy differences between first singlet and triplet excited states [14]. Therefore, we expect a marked difference in the photophysical properties for 4BGIPN, vide infra.

Analysis of the intermolecular interactions revealed that 4BGIPN molecules experience face to face intermolecular $\pi-\pi$ stacking interactions between the benzoguanidine moieties similar to 4CzIPN (reported by Etherington et al., [12]). The average interplanar distance for close neighbor benzoguanidine moieties in 4BGIPN is 3.322(3) Å, which is significantly shorter (0.4 Å) than the 3.74(3) Å average distance between nearest neighbor carbazole ligands in 4CzIPN, indicative for much stronger intermolecular interactions.

Cyclic voltammetry was used to analyze the redox behavior of 4BGIPN in THF solution containing [$n$-Bu$_4$N]PF$_6$ as supporting electrolyte (Figure 3, Table 1). The reduction wave has a quasi-reversible character with the $E_{1/2}$ at $\sim$1.50 V, which is 260 mV shifted to higher potential when compared with 4CzIPN ($\sim$1.76 V) under similar conditions in THF [15].
Table 1: Formal electrode potentials (peak position $E_p$ for irreversible and $E_{1/2}$ for quasi-reversible processes (*), $V$, vs FeCp$_2$), onset potentials ($E_{1st}$, $E_{onset}$, $V$, vs FeCp$_2$), peak-to-peak separation in parentheses for quasi-reversible processes ($\Delta E_p$ in mV), $E_{HOMO}$/$E_{LUMO}$ (eV) and band gap values ($\Delta E$, eV) for the redox changes exhibited by 4BGIPN.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Reduction</th>
<th>$E_{LUMO}$ eV</th>
<th>Oxidation</th>
<th>$E_{HOMO}$ eV</th>
<th>$\Delta E$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4BGIPN</td>
<td>$E_{1st}$ = −1.50 (167)</td>
<td>−1.41</td>
<td>$E_{1st}$</td>
<td>+1.25</td>
<td>−6.40</td>
</tr>
<tr>
<td></td>
<td>$E_{onset}$ red</td>
<td>−3.98</td>
<td>$E_{onset}$ ox</td>
<td>+1.01</td>
<td>2.42</td>
</tr>
</tbody>
</table>

*In THF solution, recorded using a glassy carbon electrode, concentration 1.4 mM, supporting electrolyte $[n-$Bu$_4$N][PF$_6$] (0.13 M), measured at 0.1 V s$^{-1}$. Calculated according to $E_{HOMO} = -(E_{onset\; red}\; Fc/Fc^+ + 5.39)$ and $E_{LUMO} = -(E_{onset\; red}\; Fc/Fc^+ + 5.39)$ eV.

Figure 3: Full range cyclic voltammogram for 4BGIPN. Recorded using a glassy carbon electrode in THF solution (1.4 mM) with $[n-$Bu$_4$N][PF$_6$] as supporting electrolyte (0.13 M), scan rate 0.1 V s$^{-1}$.

Figure 4: UV–vis absorption spectra for compound 4BGIPN in various solvents.
very weak solvatochromic effect with increasing solvent polarity from cyclohexane to dichloromethane. This indicates only minor change of the dipole moment upon vertical excitation from $S_0$ (6.4 D) to $S_1$ (7.2 D) excited states according to the TD-DFT theoretical calculations (Table S2, Supporting Information File 1).

Table 2: UV–vis data for compounds 4BGIPN and 4CzIPN [15,17] in various solvents.

<table>
<thead>
<tr>
<th></th>
<th>DCM</th>
<th>THF</th>
<th>toluene</th>
<th>cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>4BGIPN</td>
<td>436 sh (1.5)</td>
<td>435 sh (1.8)</td>
<td>439 sh (1.4)</td>
<td>439 sh (1.9)</td>
</tr>
<tr>
<td></td>
<td>358 (9.5)</td>
<td>357 (14.2)</td>
<td>358 (10.4)</td>
<td>358 (10.5)</td>
</tr>
<tr>
<td>4CzIPN</td>
<td>448 (7) [15]</td>
<td>438 (8) [15]</td>
<td>441 (6) [15]</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The photoluminescence (PL) characteristics of 4BGIPN have been studied in methylcyclohexane solution (MCH, concentration $3.2 \times 10^{-5}$ M) and Zeonex polymer films (0.1% concentration by weight) at 298 K and 77 K, which is shown in Figure 5 with data collected in Table 3. Compound 4BGIPN exhibits a featureless yellow CT-type luminescence with $\lambda_{\text{max}} = 525$ nm.
narrowing upon cooling to 77 K, while the PL profile remained triplets. The emission profiles experienced minor changes for the TADF mechanism and attempt to characterize LE and CT delays for 4BGIPN.

We collected steady state luminescence and PL after long time delays, vide supra. The energy gap for 4BGIPN, compared with 4CzIPN, indicates that the use of a larger benzoguanidine donor ligand may canteing that the use of a larger benzoguanidine donor ligand may cate the TADF luminescence mechanism. PLQY in Zeonex films is 39% in air, which is lower than the PLQY of 87% reported for 4CzIPN.

The two-component excited state lifetime with prompt and delayed fluorescence is characteristic for the TADF-type luminescence [1]. The excited state lifetime of 4BGIPN has a biexponential decay with a prompt fluorescence $\tau_p = 13$ ns and a delayed fluorescence $\tau_d = 1655$ ns components in MCH solution. Zeonex films of 4BGIPN exhibit a similar prompt fluorescence lifetime of 12 ns, but an almost two-fold longer delayed fluorescence lifetime of 2.4 ms when compared to MCH solution. The archetype material 4CzIPN possesses a similar prompt fluorescence component of 8 ns, whereas a delayed component is nearly ten-times longer, 8.9 and 8.8 ms, in MCH and Zeonex films, respectively [12]. These measurements correlate well with lower PLQY values for 4BGIPN compared with 4CzIPN, thus indicating that the use of a larger benzoguanidine donor ligand may open more nonradiative processes. This is reflected in the larger distribution in the torsion angles for 4BGIPN compared with 4CzIPN, vide supra.

We collected steady state luminescence and PL after long time delays for 4BGIPN at 77 K to further support the assignment of the TADF mechanism and attempt to characterize LE and CT triplet states. The emission profiles experienced minor narrowing upon cooling to 77 K, while the PL profile remained broad and featureless (Figure 5) in Zeonex matrices. Notably, a frozen MCH glass exhibits a new vibronically resolved component at 405 and 470 nm, together with a broad CT profile. The first resolved high-energy PL component at 405 nm (Figure 5 top right) has a lifetime of 13 ns, which we assigned to singlet locally excited fluorescence (1LE) from the benzoguanidine donor ligand. The second high-energy PL component at 470 nm becomes visible only after a long-time delay (720 ms, see Figure 5 black profile), therefore, we ascribed it to a phosphorescence from a higher lying 3LE state localized on a donor benzoguanidine moiety. Unlike 1LE-fluorescence, 3LE-phosphorescence has a very long lifetime of 1.8 s. Excitation spectra of the broad and resolved bands for 4BGIPN in MCH glass at 77 K (Figure S4, Supporting Information File 1) follow a mirror image rule when compared with emission spectra showing both broad and resolved components, thus supporting the assignments of the 3CT and 3LE(donor) excited states. The excited state lifetime of the broad CT component has a multieponential decay with averaged lifetimes of 0.7 ms in MCH glass and up to 212 ms in Zeonex films, which we assigned as phosphorescence from a 3CT state. A more than 100-fold increase in radiative lifetime on cooling to 77 K is characteristic for the organic TADF emitters [1]. Upon cooling Zeonex matrices of 4BGIPN from 296 K to 16 K (Figure 5), the excited state lifetime shows an order of magnitude increase down to 60 K. However, only marginal increase of lifetime measured in the range of 60 to 16 K indicating a phosphorescence PL nature below 60 K.

The charge transfer singlet (1CT) and local excited singlet (1LE), triplet (3LE) state energies were estimated from the onset values of the blue emission edge of the PL spectra at 295 K for 1CT and 720 ms delayed PL at 77 K for 3LE, respectively.

<table>
<thead>
<tr>
<th>λ_em (nm)</th>
<th>τ (ns)</th>
<th>$\Phi$ (%)</th>
<th>$k_r$ (10$^5$ s$^{-1}$)</th>
<th>$k_c$ (10$^5$ s$^{-1}$)</th>
<th>$\lambda$_em (nm)</th>
<th>τ</th>
</tr>
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<tbody>
<tr>
<td>methylcyclohexane (MCH) solution 296 K</td>
<td>512</td>
<td>13 (50%)</td>
<td>5.48</td>
<td>6.43</td>
<td>13 ns</td>
<td>1.8 s</td>
</tr>
<tr>
<td>4BGIPN</td>
<td>46 (N2)</td>
<td>(18 air)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2023 (75%)</td>
<td>470 (5LE); 530 (3CT)</td>
<td>13 ns</td>
<td>126 (36%) μs</td>
<td>1038 (64%) μs</td>
<td></td>
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</tr>
<tr>
<td>0.1 wt % Zeonex matrix 296 K 16 K</td>
<td>517</td>
<td>12 (35%)</td>
<td>39</td>
<td>2.56</td>
<td>4.0</td>
<td>–/–2.66</td>
</tr>
<tr>
<td>2023 (75%)</td>
<td>405 (1LE); 126 (36%) μs</td>
<td>1038 (64%) μs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4BGIPN</td>
<td>3.12/2.73/2.70</td>
<td>405 (1LE); 470 (5LE); 530 (3CT)</td>
<td>498</td>
<td>4.35 (31%) ms</td>
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<tr>
<td>512</td>
<td>6.43/5.48</td>
<td></td>
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<td>126 (36%) μs</td>
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<td>6.43/5.48</td>
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<td>1038 (64%) μs</td>
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| 481 and 500 nm in Zeonex and MCH, respectively) [12]. The solution photoluminescent quantum yield (PLQY) of 4BGIPN is 46% under inert atmosphere and decreases down to 18% in aerated MCH solution. The reduction in quantum yield on exposure to oxygen is due to quenching of the triplet excited states indicating a TADF luminescence mechanism. PLQY in Zeonex films is 39% in air, which is lower than the PLQY of 87% reported for 4CzIPN [17].

that is 44 and 25 nm red-shifted compared to 4CzIPN ($\lambda_{max} = 481$ and 500 nm in Zeonex and MCH, respectively) [12]. The solution photoluminescent quantum yield (PLQY) of 4BGIPN is 46% under inert atmosphere and decreases down to 18% in aerated MCH solution. The reduction in quantum yield on exposure to oxygen is due to quenching of the triplet excited states indicating a TADF luminescence mechanism. PLQY in Zeonex films is 39% in air, which is lower than the PLQY of 87% reported for 4CzIPN [17].
Figure 6: Energy state diagram and natural transition orbitals HONTO and LUNTO for compound 4BGIPN in excited S₁, T₁, T₂ and T₃ states calculated from the crystal S₀ geometry.

Conclusion

We have synthesized and characterized a donor–acceptor-type thermally activated delayed fluorescent emitter 4BGIPN with four terminal benzoguanidine donor moieties surrounding the benzonitrile acceptor core. We found that the material is formed as a mixture of the rotational isomers that do not experience interconversion upon heating the 4BGIPN solution in DMSO to 120 °C. Two rotational isomers were successfully crystallized to show different up and down orientations of the benzoguanidine donor ligands around the central 4,6-dicyanobenzene core. Unlike the 4CzIPN compound, the 4BGIPN emitter can crystallize in a chiral P2₁ space group due to the parallel and antiparallel orientation of the benzoguanidine donors with respect to each other, lack of C₂ rotational symmetry and extended π-conjugation. The twisted structure of the 4BGIPN ensures that the donor groups accommodate the highest occupied molecular orbital (HOMO) while the acceptor 4,6-dicyanobenzene moiety contains the lowest unoccupied molecular orbital (LUMO) and is supported by the TD-DFT calcula-
tions. A comparison of the electronic parameters between benchmark 4CzIPN and new 4BGIPN materials revealed that benzoguanidine acts as a weaker donor ligand compared with carbazole, resulting in greater stabilization of the HOMO energy level down to ~6.4 eV rather than LUMO. The significant stabilization of both HOMO and LUMO energy levels, along with multiple electron-withdrawingaza-nitrogen atoms in the structure of 4BGIPN, suggests its potential suitability as an electron transport layer in OLED (organic light-emitting diode) devices. Variable temperature photoluminescence studies revealed that 4BGIPN corresponds to the class III TADF system ($E_{3LE} > E_{1CT}$), while having a small energy difference between singlet and triplet excited states of ~0.03 eV for $\Delta E_{1CT,3LE}$. Theoretical calculations support the fact that the first three triplet excited states possess a mixed CT/LE character while benzoguanidine singlet LE state is up to 0.4 eV higher in energy than the singlet CT state. The high quantum yields of up to 46% indicate that the yellow-green 4BGIPN emitter shows a high promise as a platform for developing bright 4BGIPN-TADF class III type compounds with unity PLQY. Future works may benefit in isolating a particular isomer that could show superior photophysical TADF characteristics important for fabricating TADF OLED devices with improved operating stability.

**Experimental**

**General considerations**

All reactions were performed under a N$_2$ atmosphere. Solvents were dried as required. Sodium hydride was washed from mineral oil with diethyl ether and dried prior to use. 5H-Benzo[d][benzo[4,5]imidazo[1,2-a]]imidazole (benzoguanidine) was obtained according to the literature protocol [10] while 2,4,5,6-tetrafluoroisophthalonitrile was purchased from Fluorochem Ltd. and used as received. $^1$H and $^{13}$C NMR spectra were recorded using a Bruker AVIII HD 500 MHz NMR spectrometer. $^1$H NMR spectra (500.19 MHz) and $^{13}$C ($^{1}$H) (125.79 MHz) were referenced to dichloromethane-$d_2$ at $\delta$ 5.32 ($^{13}$C, $\delta$ 53.84). All electrochemical experiments were performed using an Autolab PGSTAT 302N computer-controlled potentiostat. Cyclic voltammetry (CV) was performed using a three-electrode configuration consisting of a glassy carbon macrodisk working electrode (GCE) (diameter of 3 mm; BASi, Indiana, U.S.A.) combined with a Pt wire counter electrode (99.99%; GoodFellow, Cambridge, U.K.) and an Ag wire pseudoreference electrode (99.99%; GoodFellow, Cambridge, U.K.). The GCE was polished between experiments using alumina slurry (0.3 μm), rinsed in distilled water and subjected to brief sonication to remove any adhering alumina microparticles. The metal electrodes were then dried in an oven at 100 °C to remove residual traces of water, the GCE was left to air dry and residual traces of water were removed under vacuum. The Ag wire pseudoreference electrodes were calibrated to the ferrocene/ferrocnium couple in THF at the end of each run to allow for any drift in potential, following IUPAC recommendations [16]. All electrochemical measurements were performed at ambient temperature under an inert N$_2$ atmosphere in THF containing the complex under study (0.14 mM) and the supporting electrolyte [n-Bu$_4$N][PF$_6$] (0.13 mM). Data were recorded with Autolab NOVA software (v. 1.11). Thermogravimetric analysis was performed by the Microanalysis Laboratory at the University of Manchester. Mass spectrometry data were obtained by the Mass Spectrometry Laboratory at the University of Manchester.

**Synthesis of 4BGIPN.** 5H-Benzo[d][benzo[4,5]imidazo[1,2-a]]imidazole (benzoguanidine, [10]) (700 mg, 3.38 mmol) was added to a suspension of NaH (81.0 mg, 3.38 mmol) in anhydrous DMF (40 mL) at 0 °C under a stream of N$_2$. The reaction mixture was stirred for 1 h at room temperature. 2,4,5,6-Tetrafluoroisophthalonitrile (135 mg, 676 μmol) was added to the reaction mixture under N$_2$. The reaction mixture was heated to 140 °C and left to stir overnight. The reaction mixture was dried under vacuum to remove DMF. The crude product was extracted with DCM and washed with water. The organic phase was collected and dried with MgSO$_4$, filtered and concentrated under vacuo. The product was further purified by column chromatography (ethyl acetate/hexane 1:4) to give the pure product as a yellow powder in 70% yield (450 mg, 474 μmol). Single crystals suitable for X-ray diffraction were grown by layering a concentrated solution in DCM with hexane which was left for slow evaporation. $^1$H NMR (700 MHz, DMSO-d$_6$) δ 8.46–8.35 (m), 8.23–8.22 (m), 8.16–8.06 (m), 7.94–6.86 (m), 6.82–6.80 (m), 6.59–6.54 (m), 6.47–6.41 (m), 6.35–6.29 (m), 6.24–6.23 (d, $J = 7.9$ Hz); $^{13}$C ($^{1}$H) NMR (126 MHz, CD$_2$Cl$_2$) δ 151.17, 149.67, 146.84, 146.65, 146.27, 144.42, 142.29, 142.01, 134.45, 133.78, 133.00, 132.63, 131.91, 130.98, 128.91, 128.50, 127.82, 126.78, 126.58, 126.41, 126.24, 125.84, 124.85, 124.51, 124.39, 124.22, 124.11, 124.01, 123.82, 123.71, 123.53, 123.38, 123.30, 123.23, 122.97, 122.76, 121.99, 121.91, 121.61, 121.41, 121.28, 120.01, 119.91, 119.68, 119.43, 119.16, 117.13, 112.60, 112.41, 112.06, 112.00, 111.69, 111.33, 111.21, 111.11, 110.88, 110.82, 110.74, 110.44, 110.17 ppm; Anal. calcd. for C$_{32}$H$_{31}$N$_{14}$ (948.29): C, 75.94; H, 3.40; N, 20.66; found: C, 75.59; H, 3.54; N, 20.28; HRESIMS m/z: [M + Na]$^+$ calcd. for C$_{60}$H$_{33}$N$_{14}$Na, 971.2827; found, 971.2854.

**X-ray crystallography**

Crystals suitable for X-ray diffraction study were obtained by slow layer diffusion of hexanes/petroleum ether into dichloromethane solution for 4BGIPN at room temperature. Crystals were mounted in oil on a MiTeGen loop and fixed on the diffractometer in a cold nitrogen stream. Data were collected
TD-DFT calculations were performed to elucidate the nature of the excited state in a crystalline and optimized molecular geometry of 4BGIPN with all data collected in Supporting Information File 1 (Tables S1–S4). All calculations were carried out by Gaussian 16 [29] and HOMO–LUMO overlap integrals were calculated using Multiwfn program [30].

For the final refinement, the contribution of severely disordered CH₃Cl₂ molecules in the crystals of 4BGIPN was accounted for by applying a solvent void mask calculated using BYPASS, implemented through Olex2 [23]. Structures were solved by direct method/intrinsic phasing and refined by the full-matrix least-squares against F². All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with C–H = 0.95–1.00 Å, and Uiso = 1.2–1.5 Ueq (parent atom). All calculations were performed using the SHELXL software and Olex2 graphical user interface [22,23].

4BGIPN (monoclinic P2₁), CCDC number 2243340, C₆₀H₇₂N₁₄, monoclinic, space group P2₁ (no. 4), a = 17.4217(4) Å, b = 15.2552(3) Å, c = 20.8314(6) Å, β = 114.583(3)°, V = 5034.6(2) Å³, Z = 4, dcalc = 1.252 g cm⁻³, µ = 0.623 mm⁻¹, yellow block, 33714 reflections measured (4.664° ≤ 2θ ≤ 152.79°), 17837 unique (Rint = 0.0314, Rsigma = 0.0512) which were used in all calculations. The final R₁ was 0.0462 (I > 2σ(I)) and wR₂ was 0.1190 (all data). GOF = 1.042, Δρmin/Δρmax = 0.4/–0.2 e Å⁻³

4BGIPN (triclinic P₁), CCDC number 2287367, C₆₀H₇₂N₁₄·0.5CH₃Cl₂ (M = 991.46 g/mol): triclinic, space group P-1 (no. 2), a = 12.8390(16) Å, b = 21.536(3) Å, c = 23.149(5) Å, α = 65.321(17)°, β = 82.509(14)°, γ = 89.955(11)°, V = 5756.1(19) Å³, Z = 4, T = 100.00(13) K, µ(Cu Kα) = 0.981 mm⁻¹, dcalc = 1.144 g/cm³, 68407 reflections measured (4.244° ≤ 2θ ≤ 151.924°), 22637 unique (Rint = 0.1849, Rsigma = 0.1991) which were used in all calculations. The final R₁ was 0.2870 (I > 2σ(I)) and wR₂ was 0.6519 (all data).

Computational results

Computations were performed using density functional theory (DFT) for the ground state and time-dependent DFT (TD-DFT) with Tamm–Dancoff approximation [24,25] for the excited states calculations, using the global hybrid MN15 functional by Truhlar [26] in combination with the def2-TZVP basis set by Ahlrichs [27,28]. TD-DFT calculations were performed using computational resources (urn:nbn:fi:research-infras-2016072533). A.S.R. made possible by use of the Finnish Grid and Cloud Infrastructure resources (urn:nbn:fi:research-infras-2016072533). A.S.R. acknowledges the support from the EPSRC (grant code EP/K039547/1).

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