Synthesis and properties of $D-\pi-A$ structural imidazole-triphenylamine derivatives

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Four novel $D-\pi$ -A structural 1-aryl-2-[4-(*N*,*N*-diphenyl]-4,5-diphenyl-1*H*-imidazoles have been synthesised. Their synthesis, thermal stability, optical properties and electrochemical behaviour have also been investigated. These compounds exhibit increased thermal stability, blue emissions and intramolecular charge transfer. The HOMO and LUMO energy levels of these compounds were calculated from electrochemical measurements.

Keywords: donor-acceptor, triphenylamine, imidazole, optical spectra, cyclic voltammetry

Organic optical functional materials have received considerable attention from both science and industry owing to their potential applications in chemistry, physics, materials science and the life sciences. Donor–acceptor π -conjugated (D– π –A) organic molecules bearing both electron-donating and electron-accepting moieties linked by a π -conjugated bridge are an important class of organic functional materials, which exhibit intramolecular charge transfer (ICT) from the donor to the acceptor moiety.¹ Indeed, numerous D– π –A structural organic molecules have been synthesised and widely used in solar cells,² organic light emitting diodes (OLEDs),³ nonlinear optics (NLO)⁴ and fluorescence sensors.⁵

Triphenylamines have been widely utilised as organic optical materials due to their high triplet energies, as well as possessing good hole-transporting and strong electron-donating properites.^{6,7} Imidazole derivatives are electron acceptors and have been proved to be efficient for electron injection and transport.^{8,9} So far, several outstanding D– π –A structural imidazole-triphenylamine derivatives have been reported for applications in various fields.^{10–12}

In this paper, we report the design and synthesis of four novel D– π –A structural 1-aryl-2-[4-(*N*,*N*- diphenyl)phenyl]-4,5-diphenyl-1*H*-imidazoles (**2a–d**). Their synthesis, thermal stability, optical properties and electrochemical behaviour have also been investigated.

Results and discussion

The 4-(diphenylamino)benzaldehyde (1) was prepared by the Vilsmeier–Haack formylation reaction using previously reported procedures (Scheme 1).¹³ Compounds **2a–d** were synthesised *via* a one-pot, four-component condensation reaction of benzil, aromatic amine, **1** and ammonium acetate in refluxing ethanol. When using the same procedures to prepare **2b**, the by-product $4-\{[(4-methoxyphenyl)imino]methyl\}-N,N-diphenylaniline (3) was obtained (Scheme 2). The crystal structure of$ **3**was determined by single crystal X-ray diffraction, as shown in Fig. 1. However, <math>2-(N,N-diphenylamino)-4,5-diphenyl-1H-imidazole (**5**) was obtained in low yields instead of the desired product**4**using 4-nitrophenylamine under identical conditions (Scheme 3). As it turned out, the results of the reaction were



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Scheme 3



Table 1 Optical, thermal and electrochemical properties of 2a-d

Compounds	$\lambda_{_{abs}}\!/nm$	$\lambda_{_{em}}/nm$	E_{g}/eV	$E_{_{\rm ox}}/{\rm eV}$	$E_{\rm homo}/E_{\rm lomo}$	$T_{\rm m}/T_{\rm d}$
2a	302, 342	403	3.21	0.73	-5.13/-1.92	219/381
2b	302, 342	402	3.18	0.91	-5.31/-2.13	213/362
2c	302, 342	410	3.22	0.78	-5.18/-1.96	227/389
2d	301, 343	412	3.24	0.59	-4.99/-1.75	238/399



Fig. 2 UV-Vis absorption and fluorescence emission spectra of 2a-d.

highly dependent on the type of aromatic amine used. In the case of aromatic amines bearing electron-donating or electronneutral substituents, the expected products were produced. In contrast, for aromatic amines bearing electron-withdrawing substituents, no products were formed. According to the results, we believe that the formation of 2a-d involves twostep reactions. A Schiff base forms from the reaction of the aromatic amine with 1 in the first step, which then reacts with the 1,2-diketone in the presence of ammonium acetate to give the products 2a-d.

The thermal properties of **2a–d** were determined using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere, and their thermal data are summarised in Table 1. The results reveal that the onset decomposition temperatures of **2a–d** were in the range 362–399 °C, which indicates that they exhibit increased thermal stability and can thus be used for the construction of electronic devices. Melting transitions were observed for compounds **2a–d** heated to 300 °C, but no glass transition was found in the same temperature range. The absorption and fluorescence emission spectra of **2a–d** were measured in dichloromethane $(1 \times 10^{-5} \text{ mol L}^{-1})$, and the relevant data are presented in Table 1. As shown in Fig. 2, compounds **2a–d** showed similar absorption and fluorescence emission spectra in solution due to their similar structures. The absorption bands at about 302 nm were ascribed to the locally excited (LE) π - π *electronic transition of the triphenylamine moiety.¹⁴ The strong absorption bands at 342 nm can be assigned to the charge transfer (CT) of the π - π *electronic transition from the electron-donating triphenylamine moiety to the electron-accepting imidazole moiety. The energy gaps (E_g) of **2a–d** were calculated from the absorption band edge,¹⁵ and the results are shown in Table 1. The fluorescence emission spectra show that compounds **2a–d** all exhibit blue emissions peaking at wavelengths in the range 402–410 nm.

The electrochemical properties of **2a–d** were studied by cyclic voltammetry in dichloromethane $(1 \times 10^{-5} \text{ mol } \text{L}^{-1})$ using tetrabutylammonium hexafluorophosphate (0.1 mol L⁻¹) as electrolyte, a glassy carbon rod as the working electrode and a Ag/Ag⁺ rod as the reference electrode. As shown in Fig. 3,



Fig. 3 Cyclic voltammograms of 2a-d.

compounds **2a–d** showed reversible oxidation peaks in the range 0.59 to 0.91 V, and the oxidation peaks of **2a–d** followed the order **2b** > **2c** > **2a** > **2d**. The highest occupied molecular orbital (HOMO) energy levels of **2a–d** were estimated from the onset oxidation potentials, and the corresponding lowest unoccupied molecular orbital (LUMO) energy levels were determined from the formula $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g}$. The results are given in Table 1. Compounds **2a–d** showed few differences in their HOMO and LUMO values as a result of their similar structures.

Conclusion

We have successfully synthesised and fully characterised four novel D– π –A structural imidazole-triphenylamine derivatives. These compounds exhibited increased thermal stability and blue fluorescence emissions. The absorption spectra showed donor– acceptor interactions between the imidazole and triphenylamine moieties. HOMO energy levels in the range –4.99 to –5.31 eV and LUMO energy levels in the range –1.75 to –2.13 eV were estimated from electrochemical measurements. Applications of these compounds as organic photoactive functional materials will be investigated in future studies.

Experimental

Reagents were purchased from commercial sources and used without further purification. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 6700 infrared spectrometer. NMR spectra were recorded on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS) as internal standard. High-resolution mass spectra (HRMS) were obtained on an Agilent 6545 Q-TOF LCMS system. UV-Vis absorption and fluorescence spectra were measured on a Varian Cary 60 and a Hitachi F-7000 fluorescence spectrometer, respectively. TGA and DSC were performed on a Mettler Toledo TGA/ DSC apparatus. Cyclic voltammetry was carried out on a CHI660C electrochemical workstation.

Synthesis of 2a, 2c, 2d and 5; general procedure

A mixture of benzil (2 mmol), 4-(diphenylamino)benzaldehyde (2.0 mmol), aromatic amine (2.0 mmol), ammonium acetate (2.0 mmol) and *p*-toluenesulfonic acid (0.2 mmol) were refluxed in ethanol (10 mL). Upon completion of the reaction, the mixture was cooled to room temperature. The solid formed was filtered and recrystallised from ethanol and DMF to give the products 2a, 2c, 2d and 5.

2-[4-(N,N-Diphenylamino)phenyl]-1-(4-methylphenyl)-4,5diphenyl-1H-imidazole (**2a**): White solid, yield 40%, m.p. 219–221 °C; IR (KBr) (v_{max} /cm⁻¹): 3058, 3029, 2917, 2850, 1596, 1511, 1488; ¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 7.2 Hz, 2H, ArH), 7.30 (d, *J* = 8.8 Hz, 2H, ArH), 7.25–7.10 (m, 12H, ArH), 7.08–7.00 (m, 8H, ArH), 6.95 (d, J = 8.4 Hz, 2H, ArH), 6.90 (d, J = 8.8 Hz, 2H, ArH), 2.31 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 147.3, 146.7, 138.3, 134.4, 131.1, 130.6, 129.7, 129.6, 129.2, 128.3, 128.2, 128.1, 127.9, 127.4, 126.6, 124.9, 123.3, 122.0, 21.2; HRMS: Calcd for C₄₀H₃₂N₃ [M+H]⁺: 554.2591; found: 554.2595.

l-(*4*-*Chlorophenyl*)-2-[*4*-(*N*,*N*-*diphenylamino*)*phenyl*]-4, 5*diphenyl*-*l*H-*imidazole* (**2c**): Light-green solid, yield 33%, m.p. 226–228 °C; IR (KBr) (v_{max} /cm⁻¹): 3054, 3029, 1589, 1492; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.47 (d, *J* = 8.4 Hz, 2H, ArH), 7.41 (d, *J* = 8.8 Hz, 2H, ArH), 7.35–7.22 (m, 14H, ArH), 7.18–7.07 (m, 4H, ArH), 7.03 (d, *J* = 8.4 Hz, 4H, ArH), 6.83 (d, *J* = 9.2 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 147.1, 131.1, 130.3, 129.8, 129.6, 129.3, 128.5, 128.2, 127.4, 125.1, 123.5, 121.7; HRMS: Calcd for C₃₉H₂₉ClN₃ [M+H]⁺: 574.2045; found: 574.2040.

l-(*4*-*Bromophenyl*)-2-[*4*-(*N*, *N*-*diphenylamino*)*phenyl*]-4, 5*diphenyl*-*l*H-*imidazole* (**2d**): Light-yellow solid, yield 29%, m.p. 238–240 °C; IR (KBr) (v_{max} /cm⁻¹): 3062, 3025, 1588, 1488; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.54 (d, *J* = 8.4 Hz, 2H, ArH), 7.47 (d, *J* = 8.4 Hz, 2H, ArH), 7.35–7.22 (m, 14H, ArH), 7.18–7.07 (m, 4H, ArH), 7.03 (d, *J* = 7.6 Hz, 4H, ArH), 6.83 (d, *J* = 8.4 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 147.2, 146.8, 136.2, 132.3, 131.1, 130.3, 129.9, 129.7, 129.3, 128.5, 128.1, 127.4, 126.7, 125.0, 123.5, 122.2, 121.9; HRMS: Calcd for C₃₉H₂₉BrN₃ [M+H]⁺: 618.1539; found: 618.1542.

2-[4-(*N*,*N*-Diphenylamino)phenyl]-4,5-diphenyl-1H-imidazole (**5**): Light-yellow solid, yield 18%, m.p. 262–263 °C; IR (KBr) (v_{max} /cm⁻¹): 3055, 3029, 1591, 1490; ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.57 (s, 3H, NH); 7.97 (d, *J* = 8.8 Hz, 2H, ArH), 7.54–7.42 (m, 6H, ArH), 7.38–7.22 (m, 8H, ArH), 7.11–7.03 (m, 8H, ArH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ 147.8, 147.3, 146.0, 130.4, 130.2, 130.0, 129.1, 128.8, 128.7, 128.6, 127.6, 127.3, 126.9, 125.9, 124.8, 124.0, 122.9; HRMS: Calcd for C₃₃H₂₆N₃ [M+H]⁺: 464.2121; found: 464.2110.

Synthesis of 2b and 3

Compounds **2b** and **3** were prepared using a similar approach to that used for **2a**. The solid obtained was separated using DMSO to give the products **2b** and **3**.

2-[4-(*N*,*N*-Diphenyl]phenyl]-1-(4-methoxyphenyl)-4,5-diphenyl-IH-imidazole (**2b**): White solid, yield 43%, m.p. 212–214 °C; IR (KBr) (v_{max} /cm⁻¹): 3037, 2958, 2830, 1587, 1513, 1488; ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 7.2 Hz, 2H, ArH), 7.32 (d, *J* = 8.8 Hz, 2H, ArH), 7.24–7.11 (m, 12H, ArH), 7.09–6.98 (m, 8H, ArH), 6.91 (d, *J* = 8.8 Hz, 2H, ArH), 6.77 (d, *J* = 9.2 Hz, 2H, ArH), 3.77 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 147.2, 131.1, 130.8, 129.7, 129.4, 129.3, 128.3, 128.1, 127.9, 127.5, 124.9, 123.4, 121.9, 114.2, 55.3; HRMS: Calcd for C₄₀H₃₇N₃O [M+H]⁺: 570.2540; found: 570.2537.

4-[[(4-Methoxyphenyl)imino]methyl]-N,N-diphenylaniline (**3**): Yellow crystals, yield 16%, m.p. 131–133 °C; IR (KBr) (v_{max} /cm⁻¹): 3052, 3027, 2909, 2839, 1585, 1510, 1485; ¹H NMR (400 MHz, DMSO- d_c): δ 8.38 (s, 1H, =CH), 7.72 (d, J = 8.4 Hz, 2H, ArH), 7.31–7.21 (m, 4H, ArH), 7.21–7.07 (m, 10H, ArH), 6.92 (d, J = 8.4 Hz, 2H, ArH), 3.82 (s, 3H, OCH₃);

Table 2 Crystal data and structure refinement parameters for 3

Empirical formula	$C_{26}H_{22}N_{2}O$		
Formula weight	378.45		
Temperature	296(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	<i>P</i> 2 ₁		
Unit cell dimensions	$\begin{array}{l} a=8.9674(12) \ \ \ \dot{A}, \alpha=90^{\circ} \\ b=9.9579(12) \ \ \dot{A}, \beta=98.914(4)^{\circ} \\ c=11.6957(15) \ \ \dot{A}, \gamma=90^{\circ} \end{array}$		
Volume	1031.8(2) Å ³		
Z, Calculated density	2, 1.218 mg m ⁻³		
Absorption coefficient μ	0.075 mm⁻¹		
<i>F</i> (000)	400		
Crystal size	0.22 × 0.20 × 0.18 mm		
Theta range for data collection	1.762 to 25.419°		
Limiting indices	$-10 \le h \le 9, -11 \le k \le 11, -14 \le l \le 14$		
Reflections collected/unique	6758/3642 [<i>R</i> (int) = 0.0429]		
Completeness to theta = 25.242	100.0		
Data/restraints/parameters	3642/2/263		
Goodness-of-fit on <i>F</i> ²	0.914		
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	$R_1 = 0.0586, wR_2 = 0.1381$		
R indices (all data)	$R_1 = 0.1155, wR_2 = 0.1759$		
Largest diff. peak and hole	0.121 and -0.183 eV Å ⁻³		

¹³C NMR (100 MHz, CDCl₃): δ 157.9, 157.8, 150.5, 146.9, 145.4, 129.8, 129.6, 129.4, 125.3, 123.9, 122.0, 121.7, 114.3, 55.5; HRMS: Calcd for $C_{26}H_{23}N_2O$ [M+H]⁺: 379.1805; found: 379.1806.

Crystal structure determination of 3

A suitable crystal of **3** was selected for single crystal X-ray diffraction analysis on a Bruker AXS Kappa APEX II diffractometer equipped with a CCD detector. The structure was solved by direct methods using the SHELXS program and refined by full-matrix least-squares techniques on F^2 using the SHELXL program. All hydrogen atoms were generated geometrically. The absolute structure could not be determined. The experimental data and refinement parameters are summarised in Table 1. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC: 1571568).

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