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Synthesis and opto-electrochemical properties of tribenzo[*a*,*c*,*i*]phenazine derivatives for hole transport materials[†]

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In this work, five novel 3,6-disubstituted-tribenzo[*a,c,i*]phenazine (2–6) derivatives were synthesized in good yield by employing a palladium catalyzed C–N bond forming amination reaction and fully characterized. Photophysical properties of 2–6 were studied both in solvent and neat solid film by UV-vis absorption, fluorescence spectroscopy and electrochemical properties by cyclic voltammetry. Absorption spectra of 2–6 showed intramolecular charge transfer (ICT) transitions in the range of 460–512 nm in solution. The HOMO and LUMO energy levels of 2–6 are in the range of –5.18 to –5.35 eV and –3.06 to –3.17 eV respectively with electrochemical bandgap within the range of 2.12–2.29 eV. HOMO energy levels of 2–6 are comparable with most commonly used hole transporting materials such as TPD, α -NPD and spiro-OMe-TAD *etc.* and thus make them potential candidates for the hole transporting material in organic electronics.

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Introduction

Tremendous progress have been made over the past few decades from industry to academia in the development of organic π -conjugated molecules bearing donor-acceptor (D-A) architecture and organic polymers, due to their potential application in organic electronics which includes organic light emitting devices (OLEDs),1-3 organic field effect transistors (OFETs),4 organic photovoltaics (OPVs)5-7 etc. Compared to organic polymers, small organic π -conjugated molecules have great advantages in terms of high luminescence quantum yield,^{8,9} well defined structures, ease of purification, reliable reproducibility, better solubility in most organic solvents and easy fabrication of devices.¹⁰⁻¹³ Owing to their unique charge transfer properties, it is possible to tune the electro-optical properties of D-A type molecules by modifying donoracceptor moieties.9,14 In the recent past a variety of D-A type molecules exhibiting interesting electro-photophysical and thermal properties based on anthracene,15,16 benzimidazole,17 carbazole,18,19 dibenzothiophene,20 fluorene,21,22 pyrene23,24 and quinoxaline²⁵⁻³⁴ have been synthesized and some of them have been utilized as electroluminescent materials in organic electronic devices.

Hole transporting materials (HTMs) are common in small organic molecules based OLEDs and play pivotal role in the performance and durability of a devices. Molecules with lower ionization potential and lower electron affinities *i.e.* material with electron donating properties serve as HTMs.1 The main function of HTMs is to transfer the positive charge carriers (hole) to the emitting layer. So far number of aromatic amine derivatives have been reported and utilized for HTMs includes NPD (N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,10biphenyl)-4,4'-diamine),^{1,35} TPD (N,N'-bis(3-methylphenyl)-N,N'diphenylbenzidine),³⁶ spiro-OMe-TAD (2,2',7,7'-tetrakis[N,Ndi(4-methoxyphenyl)amino]-9,9'-spirobifluorene),37-40 Shirota star shaped molecules41,42 and oligomeric amines43 etc. However, due to low thermal stability of certain HTMs such as **TPD** and NPD (both having low glass transition temperature (T_{g}) of 65 °C and 95 °C respectively)44 large scope is there for the other organic materials to act as alternatives for the above mentioned commonly used hole transporting materials, as low thermal stability is lethal to the efficiency and durability of the devices. Thus, organic material with lower HOMO, LUMO energy levels and high thermal stability are much sought for HTMs. In literature recently Z. Wang et al. (2013) reported application of triphenylamine based on tribenzo[a,c,i]phenazine derivatives in photovoltaics.45 Thus in this work, keeping in mind importance of D-A type of molecules and hole transporting materials in organic electronics, we designed and synthesized compounds 2-6 by incorporating Buchwald-Hartwig coupling amination reaction46,47 between electron deficient 3,6-dibromotribenzo [a,c,i] phenazine (1) and various electron donating diarylamines (2-5) and morpholine (6) at 3rd and 6th positions of 1 and studied their detailed optoelectronic and thermal properties.

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Paper

The design of compounds **2–6** is mainly based on the fact that the diarylamines are well known electron donors and compound **1** is selected as an electron deficient backbone due to the presence of imine nitrogen atom and its coplanar structure formed by connecting two separated phenyl ring of phenylsubstituted quinoxaline derivatives with a single bond between the *ortho* positions.⁴⁸ In compound **6** we have used morpholine amine to see effect of a cyclic aliphatic amine on the photoelectrochemical and thermal properties of tribenzo[*a*,*c*,*i*]phenazine. Further, the studies also explore the effect of electron donating and withdrawing substituents on the diarylamine moiety on the photophysical and the electrochemical properties such as intramolecular charge transfer transitions (ICT), HOMO-LUMO energy levels and energy band gap. The structures of the synthesized molecules **2–6** are shown in Fig. 1.

Results and discussion

Synthesis and characterization

Compound **1** (3,6-dibromotribenzo[a,c,i]phenazine) was synthesized by condensing 3,6-dibromophenanthrene-9,10dione (7) and 2,3-diaminonaphthalene in glacial acetic acid



6

Fig. 1 Molecular structures of compounds 2–6.

with 89% yield. Compound 7 was prepared according to reported procedure with 86% yield and confirmed by its melting point 288 °C (lit. 286-287 °C).49 Compounds 2-6 were obtained by the Buchwald-Hartwig coupling47,48 of 1 with the corresponding diarylamine (2-5) and morpholine (6) in the presence of palladium catalyst, ligand and strong base in tetrahydrofuran (THF) (Scheme 1). Other solvents such as toluene and dimethyl sulfoxide (DMSO) were also tried, but best results are obtained in THF in terms of yield and reaction time. Tris(dibenzylideneacetone)dipalladium $(Pd_2(dba)_3)$ was a source of catalyst. Ligands such as 2-dicyclohexylphoshpino-2',6'-dimethoxybiphenyl (SPhos), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XantPhos) and 1,1'-bis(diphenyl phosphino)ferrocene (DPPF) were also used. Sodium tertiary butoxide (t-BuONa) as a base was used. However, the use of Pd₂(dba)₃/SPhos catalyst-ligand combination with base t-BuONa significantly reduces the reaction time with good yield.

Further it is worth to mention that no coupling reaction was observed when diarylamines bearing functional group such as amino $(-NH_2)$ and nitro $(-NO_2)$ and heteroamines such as phenothiazine, phenoxazine and carbazole were used in the reaction. The synthesized compounds **2–6** were obtained in 54–69% yield as dark orange to dark red to brown solids soluble in common organic solvents including dichloromethane, toluene,

methanol and cyclohexane. However, they are completely insoluble in water. The identity and purity of all the target compounds were confirmed by FT-IR, ¹H and ¹³C NMR spectroscopy, high resolution mass spectroscopy (HRMS) and elemental analysis. The synthetic route of compounds **2–6** is shown in Scheme **1**.

Photophysical properties

The optical properties of compounds **2–6** were investigated by UV-visible and fluorescence spectroscopy. In order to understand the charge transfer characteristic and effect of solvent polarity on the photophysical properties of **2–6**, their optical properties were measured in solvents with varying polarity (cyclohexane, toluene, dichloromethane, methanol and dimethyl sulfoxide) and neat solid film. The synthesized molecules show similar UV-vis absorption spectra in all above solvents and neat solid film (Fig. 2).

The compound **1** (see ESI[†]) shows two absorption maxima at 310 and 323 and lower intensity peaks at 405 and 429 nm respectively in toluene which are due to $n-\pi^*$ and $\pi-\pi^*$ transitions. The absorption spectra of **2–6** in all mentioned solvents show major bands around 300–355 nm corresponding to $n-\pi^*$, $\pi-\pi^*$ transitions. Apart from $n-\pi^*$, $\pi-\pi^*$ transition,



Scheme 1 Synthetic route of 2-6.

Paper



Fig. 2 UV-vis absorption spectra of compounds 2-6 in toluene (a) and neat solid film (b) (for other solvents see ESI[†]).

synthesized compounds also show lower intensity (energy) transition around 460–512 nm (Table 1).

This lower intensity transition are attributed to intramolecular charge transfer (ICT) transitions from various electron donor arylamines in 2–5 and morpholine in 6 to electron acceptor tribenzo[a,c,i]phenazine segment (Fig. 2). It is this lowest-energy absorption band that is most sensitive to the solvent polarity and to the donor moiety. However no

Table 1 Absorption data of compounds 2–6								
Compd	$\lambda_{\rm abs}{}^a$, nm (log $\varepsilon_{\rm max}$ M ⁻¹ cm ⁻¹)							
	Toluene	Cyclohexane	CH_2Cl_2	CH ₃ OH	DMSO	Film		
2	323 (4.80), 491 (4.41)	320 (4.94), 467 (4.53), 496 (4.59)	322 (4.89), 491 (4.50)	319 (4.64), 488 (4.24)	325 (4.89), 495 (4.52)	348, 520		
3	321 (5.13), 492 (4.42)	319 (4.87), 492 (4.53), 495 (4.59)	320 (4.99), 488 (4.61)	320 (4.75), 487 (4.08)	321 (4.90), 492 (4.58)	339, 510		
4	327 (5.05), 509 (4.70)	325 (4.79), 512 (4.46)	325 (5.04), 508 (4.70)	322 (4.20), 505 (3.79)	328 (4.60), 508 (4.64)	363, 521		
5	322 (4.91), 492 (4.67)	319 (4.87), 471 (4.61), 497 (4.65)	320 (4.85), 486 (4.60)	320 (4.63), 487 (4.28)	320 (4.60), 492 (4.38)	325, 446, 492		
6	304 (4.97), 464 (4.54)	300 (4.93), 347 (4.58), 460 (4.97)	304 (4.80), 465 (4.37)	301 (4.91), 340 (4.51), 462 (4.46)	307 (5.01), 355 (4.66), 476 (4.60)	316, 489		

^{*a*} Recorded in 10^{-5} M solution.



Fig. 3 Fluorescence spectra of 2-6 in toluene (a) and neat solid film (b) (for other solvents see ESI⁺).

Table 2 Emission data, Stokes shift, optical bandgap and quantum yield of compounds 2-6

Paper

	$\lambda_{\rm emi}{}^a$, nm		$\lambda_{\rm emi}$, nm			
Compd	Toluene	Cyclohexane	Film	Stokes shift ^{<i>b</i>} , cm^{-1}	$E_{ m g}^{{ m opt}c}$ (eV)	$\phi_{ m F}{}^d$
2	555	515	585	12 941	2.35 (2.37)	0.27
3	546	512	580	12 837	2.37 (2.38)	0.11
4	616	550	636	14 347	2.15 (2.17)	0.14
5	544	_	_	_	_ ` ´	_
6	542	507	562	$14\ 444$	2.40(2.41)	0.18

form and toluene (in parentheses) $\left(E_{g}^{opt} = \frac{1240.8}{\lambda_{opt} edge}\right)$ eV. ^{*d*} Quantum yield with reference to fluorescein ($\phi = 0.79$ in ethanol) in toluene.

bathochromic shift was observed on increasing the solvent polarity on $n-\pi^*$, $\pi-\pi^*$ transition and ICT transitions in 2–6, indicating that the ground state of molecules are more stable than the excited state.

Slight red shift in ICT transition of around 13–18 nm was observed in the case of compound 4 due to the presence of electron donating methoxy (–OCH₃) group on the diarylamine moiety. However, blue shift of 18–32 nm and 19–36 nm was observed in n– π^* , π – π^* and ICT transitions respectively in compound **6** as compared to other derivatives due to the presence of aliphatic cyclic amine, morpholine. Absorption of **2–6** in neat solid film was observed in the range of 316–339 nm and 489–521 nm. Bathochromic shift observed in thin film absorption maxima and slight broadening of peak suggest the presence of intermolecular aggregation in solid state.

On excitation at λ_{max} (325 nm) obtained in absorption spectra compounds **2–6** emit in green region with emission maxima in the range of 542–616 nm (Fig. 3a). A bathochromic shift of 61–74 nm was observed in compound **4** as compared to other derivatives in toluene due to the presence of electron



Fig. 4 The cyclic voltammogram (anodic sweep) of compounds 2–4 (a) and a full scan of compound 5 (b) measured in anhydrous CH₂Cl₂.

Table 3	Electrochemical and thermal	data of compour	nds 2–6								
Compd	$E_{ m oxi}^{ m peaka}$	$E_{ m red}^{ m peakb}$	HOMO ^c	$LUMO^d$	$E_{\mathrm{g}}^{\mathrm{EC}e}$	$T_{\rm m}^{f}(^{\circ}{\rm C})$	$T_{\mathbf{d}}^{g}(^{\circ}\mathbf{C})$				
2	1.04, 1.42	-1.30	-5.35	-3.11	2.24	290	424 (460)				
3	1.03, 1.29	-1.30	-5.34	-3.13	2.21	316	255 (355)				
4	0.86, 1.43	-1.37	-5.18	-3.06	2.12	299	400 (465)				
5	1.17, 1.61	-1.30	-5.46	-3.17	2.29	297	271 (367)				
6	0.96, 1.11, 1.50	-1.38	-5.28	-3.07	2.21	358	345 (394)				

^{*a*} $E_{\text{oxi}}^{\text{peak}}$ oxidation peak potential (V). ^{*b*} $E_{\text{red}}^{\text{peak}}$ reduction peak potential (V). ^{*c*} HOMO energy level calculated from $E_{\text{HOMO}} = -[E_{\text{oxi}}^{\text{peak}} - E_{\text{redox}}(\text{Fc/Fc}^+) + 4.8] \text{ eV.}^{$ *d* $}$ LUMO energy level calculated from $E_{\text{LUMO}} = -[E_{\text{red}}^{\text{peak}} - E_{\text{redox}}(\text{Fc/Fc}^+) + 4.8] \text{ eV.}^{$ *e* $} E_{\text{g}}^{\text{EC}}$ calculated from $E_{\text{g}}^{\text{EC}} = [\text{HOMO} - \text{LUMO}] \text{ eV.}^{$ *f* $}$ Melting point determined by DSC. ^{*g*} Decomposition temperature at 5% and 10% (in parentheses) weight loss derived by TGA.

Paper



Fig. 5 Frontier molecular orbital of compounds 2–6 based on DFT (B3LYP/6-311G) calculations.

However quenching in emission was observed for 2-6 in methanol and compound 4 and 5 does not emit in CH₂Cl₂ and DMSO suggesting nonradiative relaxation from excited state to ground state in polar solvents due to presence of polar groups such as -OCH3 and diazene. Blue shift of around 34-66 nm was observed in cyclohexane as compared to toluene. Bathochromic shift of around 20-34 nm was observed as compared to toluene in the neat solid film ranging from 562–636 nm (Fig. 3b). It may be due to intermolecular aggregation in the solid state. A large Stokes shift was observed for compounds 2-6 which suggest the considerable change in the ground and excited state geometry (Table 2). The quantum yield of 2-6 were calculated using fluorescein ($\phi = 0.79$ in ethanol) as reference. Optical bandgap of 2-6 were determined by the intersection of emission and excitation spectra. Quantum yields were found to be dependent on the electron-donating nature of diarylamines at 3rd and 6th positions of tribenzo [a,c,i] phenazine backbone.

Electrochemical properties

The redox behavior and electrochemical energy levels (HOMO and LUMO) of compounds **2–6** were studied by cyclic voltammetry (CV) (Fig. 4) in anhydrous dichloromethane solution using ferrocene as an internal standard to calibrate the redox potentials and the pertinent data is presented in Table 2.

On anodic sweep two quasi-reversible waves observed for all compounds **2–6** which is attributed to the oxidation of diarylamine moiety at 3rd and 6th positions of tribenzo[a,c,i]phenazine moiety corresponding to two electrons. E_{oxi} potential of **2–6** decreases on increasing donor strength (**4** > **6** > **3** > **2** > **5**). Additional peak at 0.96 V was observed in compound **6** due to the oxidation of the morpholine group. On cathodic sweep one reversible wave observed for **2–6** (see ESI†) corresponding to the reduction of tribenzo[a,c,i]phenazine core. The energy levels of the highest occupied and lowest unoccupied molecular orbital's (HOMO and LUMO) were calculated from first oxidation and reduction potentials. The HOMO and LUMO energy levels of **2–6** are found in the range of -5.18 to -5.35 eV and -3.06 to -3.17eV respectively.

HOMO energy levels of 2–6 are comparable to the commonly used hole transporting materials such as **TPD** (HOMO = -5.12 eV),³⁶ **\alpha-NPD** (HOMO = -5.20 eV),³⁵ **spiro-OMe-TAD** (HOMO = -5.22 eV),³⁷⁻⁴⁰ 9,9-dimethyl-*N*,*N*'-di(1-naphthyl)-*N*,*N*'-diphenyl-9*H*-fluorene-2,7-diamine (DMFL-NPB) (HOMO = -5.20 eV),⁵⁰

Table 4 Computed electron affinities, ionization potentials, HOMO–LUMO energies, energy band gap and dipole moment of compounds 2-6

Compd	EA (eV)	IP (eV)	HOMO (eV)	LUMO (eV)	$E_{ m g}^{ m TH}$	$\mu_{ m g}$ (debye)
2	1.43	6.21	-5.24	-2.59	2.65	2.56
3	1.38	6.17	-5.25	-2.50	2.75	2.96
4	1.30	5.91	-4.97	-2.42	2.54	4.46
5	1.86	6.23	-5.35	-2.75	2.60	2.90
6	1.29	6.59	-5.39	-2.50	2.88	1.55



Fig. 6 TGA thermogram of compounds 2-6 (a) and DSC thermogram of compound 4 (b) under nitrogen atmosphere at normal pressure. Heating rate, 10 °C min⁻¹.

1,3,5-tris (2-(9-ethylcabazyl-3)ethylene)
benzene (HOMO = -5.20 eV) $^{\rm 51}$ etc.

The energy band gap calculated from cyclic voltammetry measurements are in the range of 2.12–2.29 eV. The decrease in the bandgap was observed in compound 4 (2.12 eV) indicating the influence of electron donating group ($-OCH_3$) on diaryl-amine moiety. Whereas in case of compound 5 (2.29 eV) the energy band gap was slightly high compared to other derivatives due to presence of electron withdrawing diazene group on diarylamine segment (Table 3).

Theoretical properties

To gain better insight into the HOMO and LUMO energy levels of compounds **2–6**, the structures and frontier molecular orbital profiles of these molecules were optimized using DFT calculations at the B3LYP/6-311G level in the Gaussian 03 suite of programs.⁵² Fig. 5 shows theoretically calculated molecular orbitals of compounds **2–6**.

Theoretically calculated HOMO and LUMO of compounds 2– 6 are in the range of -4.97 to -5.39 eV and -2.42 to -2.75 eV respectively with energy band gap from 2.54 to 2.88 eV (Table 4).

Theoretically calculated HOMO energy levels and energy bandgap of 2-6 are in close agreement with those calculated by CV. However LUMO energy levels calculated by CV are slightly higher than estimated computationally, which may be due to the interaction between the solvent and molecules. HOMO energy level of compound 2, 3 and 6 are localized throughout the molecules (Fig. 5) and in 4 and 5 it is partially located on the tribenzo[a,c,i]phenazine core and diarylamine moiety at its 3rd position. However LUMO energy levels of 2-6 are entirely located on the tribenzo [a,c,i] phenazine backbone. This clearly demonstrate that the HOMO-LUMO transitions occurring from electron donor diarylamines to electron acceptor tribenzo [a,c,i]phenazine core thus strongly support the experimental investigations. The first ionization potential, electron affinity, energies of the HOMO and LUMO levels, HOMO-LUMO gap and ground-state dipole moment computed for compounds 2-6 are collected in Table 4. Further computed dipole moment of 4

(4.46) is high as compared to other compounds due to the presence of $-OCH_3$ group on diarylamine moiety.

Thermal properties

The luminescent materials with amorphous nature and high thermal stability are suitable candidate for the HTMs. The thermal properties of compounds **2–6** was determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 6).

Melting points of **2–6** were determined by DSC (see ESI†) and are in the range of 290–358 °C. Fig. 6b show the melting point and glass phase transition temperature ($T_g = 184$ °C) of compound **4** determined by DSC. No glass phase transition was observed in compounds **2**, **3**, **5** and **6** (see ESI†). TGA thermogram (Fig. 6a) of compounds **2–6** reveal that these derivatives have good thermal stability with no weight loss at low temperature. The decomposition temperature corresponding to 5% and 10% weight losses were in the range of 255–424 °C and 355– 460 °C respectively (Table 3).

The order of thermal stability among the synthesized derivatives is 2 > 4 > 6 > 5 > 3. The stability of compound 2–6 are good and comparable to commonly used HTMs. Further glass transition temperature of compound 4 is much higher than the **TPD** $(T_g = 65 \text{ °C})$ and α -**NPD** $(T_g = 95 \text{ °C})$.⁴⁴ Thus high thermal stability of 2–6 makes them suitable in making stable amorphous film and enhances the performance and lifetime of the devices.

Conclusions

In summary, five novel 3,6-disubstituted tribenzo[a,c,i]phenazine derivatives were synthesized *via* Buchwald–Hartwig palladium-catalyzed C–N bond forming reaction using Pd₂(dba)₃/SPhos catalyst system in good yields. The electrooptical and thermal properties of the synthesized materials is significantly influenced by the nature of peripheral amines attached to the tribenzo[a,c,i]phenazine core. Lower intensity ICT transition were found in **2–6**. Compounds **2–6** emits in green region (562–636 nm) in neat solid film except **5**. The ionization potential (HOMO energy levels) of **2–6** is found in the range of -5.18 to -5.35 eV and are comparable to the commonly used/reported hole transporting materials. The theoretically obtained results are in close agreement with the experimental results. Thermal properties reveal that the derivatives have high melting point and good thermal stability. The experimental and theoretical results of **2–6** promises the use of these molecules as hole transporting materials in optoelectronic devices.

Experimental

Materials and instruments

All the starting materials and reagents were purchased from commercial sources (Sigma Aldrich and Alfa Aesar) and were used without any further treatment and purifications unless otherwise noted. The organic solvents were of HPLC and spectroscopic grade and were dried and freshly distilled using the standard procedures and handled in moisture free atmosphere. Column chromatography was carried out using SD-Fine silica gel (60–120 mesh), eluting with *n*-hexane and chloroform. The progress of reaction and the purity of the compound were checked by thin layer chromatography (TLC) on silica gel coated glass plates, in which the spots were visualized with UV light (365 nm) and in iodine chamber.

UV-visible spectra were recorded in 10^{-5} mol L⁻¹ solutions in a 1 cm path length quartz cuvette as well as the neat solid films on SHIMADZU U.V-2401PC at room temperature. The neat solid films of compounds 2-6 were prepared by using Spin coater (Holmarc HO-TH-05) at 1000 rpm for 2 min using \sim 6 mg mL⁻¹ of sample in chloroform. Quartz substrate was used for neat solid film studies. The excitation and emission spectra were carried out on a Perkin Elmer LS 55 Fluorescence spectrophotometer. Fluorescence quantum yield of the derivatives 2-6 were calculated using fluorescein ($\phi_{\rm F} = 0.79$ in ethanol). Cyclic voltammetry studies were carried out on a computer controlled Palmsens3 potentiostat/galvanostat. Typically, a three electrode cell equipped with a glassy carbon working electrode, Ag/AgCl (non-aqueous) reference electrode and platinum (Pt) wire as counter electrode was employed. The measurements have been carried at room temperature in anhydrous acetonitrile with tetra butyl ammonium hexafluorophosphate solution (0.1 M) as supporting electrolyte with a scan rate of 100 mV s^{-1} . The potential of Ag/AgCl reference electrode was calibrated by using ferrocene/ferrocenium redox couple which has the known oxidation potential of +4.8 eV.53 Melting points of the products were determined by Differential Scanning Calorimetry (DSC). The thermogravimetric analysis (TGA) and DSC was performed using Metler Toledo Instrument (TG/DSC) under nitrogen atmosphere. ¹H NMR spectra and ¹³C NMR spectra were recorded using CDCl₃ on a Bruker 300 Ultrashield spectrometer with tetramethylsilane (TMS) as internal reference at a working frequency of 300 MHz and 75 MHz respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. The spectra of solid compounds were performed in KBr pellets. High resolution mass spectrometric measurements were recorded on maxis impact 282001.00081

instrument using Bruker compass data analysis 4.1 and elemental analysis was carried on EA Euro-elemental analysis instrument.

Synthetic procedures

Synthesis of 3,6-dibromotribenzo[a,c,i]phenazine (1). A mixture of 3,6-dibromophenanthrene-9,10-dione (0.92 g, 2.5 mmol) and 2,3-diaminonaphthalene (0.40 g, 2.5 mmol) was dissolved in 25 mL of glacial acetic acid and refluxed for 5 hours. The reaction mixture was allowed to cool and then poured over crushed ice to obtain the orange coloured solid. The obtained solid was then dried under vacuum and purified using column chromatography (eluent: n-hexane : chloroform ratio as 60 : 40), orange solid, yield 1.09 g (89%); mp > 360 °C; FT-IR (KBr, ν_{max} cm⁻¹): 3033.22, 1589.33, 1425.34, 1256.33, 865.23; ¹H NMR (300 MHz, CDCl₃, δ ppm): 9.21 (2H, d, J = 9.0Hz, aromatic), 8.78 (2H, s, aromatic), 8.12 (2H, dd, J = 3.0 Hz, aromatic), 7.70 (2H, s, aromatic), 7.52 (2H, dd, J = 3.0 Hz, aromatic), 7.28 (2H, d, J = 9.0 Hz, aromatic); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 153.01, 143.70, 138.84, 133.54, 128.39, 128.14, 126.71, 126.44, 125.99, 123.19, 116.29, 107.27; MS: C₂₄H₁₂N₂Br₂, m/z: 488.05 [M]⁺; anal. calcd for C₂₄H₁₂N₂Br₂: C, 59.05; H, 2.48; Br, 32.74; N, 5.74. Found: C, 59.04; H, 2.49; Br, 32.70; N, 5.78.

General procedure for the synthesis of compounds 2-6

A mixture of compound **1** (0.130 g, 0.25 mmol) and various diarylamines (0.6 mmol) was dissolved in anhydrous tetrahydrofuran (20 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (13 mg, 0.03 mmol) and *t*-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 80 °C for 4 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: *n*-hexane : chloroform ratio as 70 : 30).

*N*³,*N*³,*N*⁶,*N*⁶-Tetraphenyltribenzo[*a*,*c*,*t*]phenazine-3,6-diamine (2). Red solid, yield: 90 mg (54%); mp 290 °C; FT-IR (KBr, ν_{max} cm⁻¹): 3084.23, 1585.90, 1487.88, 1257.59, 710.67; ¹H NMR (300 MHz, CDCl₃, δ ppm): 9.11 (2H, d, *J* = 9.0 Hz, aromatic), 8.768 (2H, s, aromatic), 8.10 (2H, dd, *J* = 3.0 Hz, aromatic), 7.55 (2H, s, aromatic), 7.51 (2H, dd, *J* = 3.0 Hz, aromatic), 7.36–7.27 (10H, m, aromatic), 7.17–7.077 (12H, m, aromatic); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 150.27, 146.80, 143.65, 138.85, 133.62, 133.29, 129.40, 128.38, 127.67, 126.79, 126.03, 125.50, 124.18, 121.86, 121.04, 114.38; HRMS calcd for C₄₈H₃₃N₄ [M + H]⁺: 665.2700, found 665.2718; anal. calcd for C₄₈H₃₃N₄: C, 87.72; H, 4.85; N, 8.43. Found: C, 86.68; H, 4.85; N, 8.47.

 N^3 , N^6 -Di(naphthalene-1-yl)- N^3 , N^6 -diphenyltribenzo[*a*,*c*,*i*] phenazine-3,6-diamine (3). Brown solid, yield: 119 mg (62%); mp 316 °C; FT-IR (KBr, ν_{max} cm⁻¹): 3055.89, 1589.09, 1235.89, 1045.15, 824.23, 723.56. ¹H NMR (300 MHz, CDCl₃, δ ppm): 9.06 (2H, d, *J* = 9.0 Hz, aromatic), 8.72 (2H, s, aromatic), 8.08 (2H, dd, *J* = 3.0 Hz, aromatic), 7.89 (4H, dd, *J* = 3.0 Hz, aromatic), 7.77 (2H, d, *J* = 9.0 Hz, aromatic), 7.48–7.02 (24H, m, aromatic); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 150.86, 147.04, 146.80, 143.69, 143.56, 142.45, 142.31, 138.82, 133.57, 133.37, 131.04, 130.98, 128.50, 128.35, 127.77, 127.44, 127.24, 126.66, 126.23, 125.95, 123.94, 123.49, 123.42, 123.27, 120.34, 112.38; HRMS calcd for $C_{56}H_{37}N_4$ [M + H]⁺: 765.3013, found 765.2998; anal. calcd for $C_{56}H_{36}N_4$: C, 87.93; H, 4.74; N, 7.32. Found: C, 87.80; H, 4.87; N, 7.32.

*N*³,*N*³,*N*⁶,*N*⁶-Tetrakis(4-methoxyphenyl)tribenzo[*a*,*c*,*i*] phenazine-3,6-diamine (4). Dark red solid, yield: 135 mg (69%); mp 299 °C; FT-IR (KBr, ν_{max} cm⁻¹): 3089.20, 2929.90, 1597.34, 1499.89, 1234.89, 823.67, 715.23; ¹H NMR (300 MHz, CDCl₃, δ ppm): 9.04 (2H, d, *J* = 9.0 Hz, aromatic), 8.73 (2H, s, aromatic), 8.09 (2H, dd, *J* = 3.0 Hz, aromatic), 7.49 (2H, dd, *J* = 3.0 Hz, aromatic), 7.45 (2H, d, *J* = 9.0 Hz, aromatic), 7.20 (2H, d, *J* = 3.0 Hz, aromatic), 7.17 (2H, d, *J* = 3.0 Hz, aromatic), 7.11 (6H, d, *J* = 9.0 Hz, aromatic), 6.83 (8H, d, *J* = 9.0 Hz, aromatic), 3.83 (12H, s, -OCH₃); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 156.58, 150.98, 143.88, 139.79, 138.85, 133.47, 133.42, 128.34, 127.64, 127.25, 126.55, 125.84, 122.87, 119.57, 114.79, 111.64, 55.42; HRMS calcd for C₅₂H₄₁N₄O₄ [M + H]⁺: 785.3122, found 785.3218; anal. calcd for C₅₂H₄₀N₄O₄: C, 79.57; H, 5.14; N, 7.14; O, 8.15. Found: C, 79.60; H, 5.11; N, 7.19; O, 8.12.

*N*³,*N*⁶-Diphenyl-*N*³,*N*⁶-bis(4-((*E*)-phenyldiazenyl)phenyl)tribenzo[*a*,*c*,*i*]phenazine-3,6-diamine (5). Dark brown solid, yield: 124 mg (57%); mp 297 °C; FT-IR (KBr, ν_{max} cm⁻¹): 3035.12, 1588.56, 1489.78, 1266.34, 1137.78, 698.45. ¹H NMR (300 MHz, CDCl₃, δ ppm): 9.17 (2H, d, *J* = 9.0 Hz, aromatic), 8.78 (2H, s, aromatic), 8.10 (2H, dd, *J* = 3.0 Hz, aromatic), 7.91 (4H, d, *J* = 7.2 Hz, aromatic), 7.88 (4H, d, *J* = 8.7 Hz, aromatic), 7.66 (2H, d, *J* = 1.8 Hz, aromatic), 7.53–7.43 (10H, m, aromatic), 7.30–7.08 (14H, m, aromatic); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 152.89, 149.50, 149.46, 148.18, 146.18, 143.37, 138.85, 133.79, 133.16, 130.51, 129.76, 129.08, 128.42, 127.90, 127.07, 126.35, 125.41, 125.24, 124.34, 124.29, 123.54, 123.15, 122.66, 116.11; HRMS calcd for C₆₀H₄₁N₈ [M + H]⁺: 873.3496, found 873.3513; anal. calcd for C₆₀H₄₀N₈: C, 82.55; H, 4.62; N, 12.84. Found: C, 82.45; H, 4.67; N, 12.89.

3,6-Dimorpholinotribenzo[*a,c,i*]**phenazine** (6). Yellow solid, yield: 76 mg (60%); mp 358 °C; FT-IR (KBr, ν_{max} cm⁻¹): 2964.48, 1586.24, 1495.94, 1210.84, 1114.03, 908.81, 793.32, 726.17, 636.97; ¹H NMR (300 MHz, CDCl₃, δ ppm): 9.16 (2H, d, *J* = 9.0 Hz, aromatic), 8.75 (2H, s, aromatic), 8.10 (2H, dd, *J* = 3.0 Hz, aromatic), 7.61 (2H, s, aromatic), 7.51 (2H, dd, *J* = 3.0 Hz, aromatic), 7.21 (2H, d, *J* = 9.0 Hz, aromatic), 3.95 (8H, t, *J* = 4.5 Hz); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 152.98, 143.67, 138.65, 133.60, 128.38, 128.15, 126.67, 125.95, 125.07, 123.18, 116.24, 107.24, 66.85, 48.70; HRMS calcd for C₃₂H₂₉N₄O₂ [M + H]⁺: 501.2285, found 501.2288; anal. calcd for C₃₂H₂₈N₄O₂: C, 76.78; H, 5.64; N, 11.18; O, 6.39. Found: C, 76.60; H, 5.83; N, 11.19; O, 6.38.

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References

- 1 C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett., 1987, 51, 913.
- R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Lögdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121.
- 3 M. A. Baldo, M. E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750.
- 4 J. E. Anthony, Angew. Chem., Int. Ed., 2008, 47, 452.
- 5 M. Grätzel, Acc. Chem. Res., 2009, 42, 1788.
- 6 H. Imahori, T. Umeyama and S. Ito, *Acc. Chem. Res.*, 2009, **42**, 1809.
- 7 Z. Ning and H. Tian, Chem. Commun., 2009, 5483.
- 8 A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556.
- 9 Y. Shirota, J. Mater. Chem., 2005, 15, 75.
- 10 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, 37, 402.
- 11 C. H. Chen and C. W. Tang, Appl. Phys. Lett., 2001, 79, 3711.
- 12 C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, 5048.
- 13 X. Zhang and S. A. Jenekhe, Macromolecules, 2000, 33, 2069.
- 14 R. R. Reghu, H. K. Bisoyi, J. V. Graulevicius, P. Anjukandi, V. Gaidelis and V. Jankauskas, *J. Mater. Chem.*, 2011, 48, 3039.
- 15 S. K. Kim, B. Yang, Y. I. Park, Y. Ma, J.-Y. Lee and K. H.-J. Park, *Org. Electron.*, 2009, **10**, 822.
- 16 B. Yang, S. K. Kim, H. Xu, Y.-I. Park, H.-Y. Zhang, C. Gu, F. Z. Shen, C. L. Wang, D. D. Liu, X. D. Liu, M. Hanif, S. Tang, W. J. Li, F. Li, J. C. Shen, J. W. Park and Y.-G. Ma, *ChemPhysChem*, 2008, 9, 2601.
- 17 M. Y. Lai, C. H. Chen, W. S. Huang, J. T. Lin, T. H. Ke, L. Y. Chen, M. H. Tsai and C.-C. Wu, *Angew. Chem., Int. Ed.*, 2008, 47, 581.
- 18 J.-Y. Shen, X.-L. Yang, T.-H. Huang, J. T. Lin, T.-H. Ke, L.-Y. Chen, C.-C. Wu and M.-C. P. Yeh, *Adv. Funct. Mater.*, 2007, 17, 983.
- 19 K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404.
- 20 T.-H. Huang, J. T. Lin, L.-Y. Chen, Y.-T. Lin and C.-C. Wu, *Adv. Mater.*, 2006, **18**, 602.
- 21 Y. S. Kwon, K. H. Lee, K. G. Young, J. H. Seo, Y. K. Kim and S. S. Yoont, *J. Nanosci. Nanotechnol.*, 2009, 9, 7056.
- 22 Z. Jiang, Z. Liu, C. Yang, C. Zhong, J. Qin, G. Yu and Y. Liu, *Adv. Funct. Mater.*, 2009, **19**, 987.
- 23 D. E. Loy, B. E. Koene and M. E. Thompson, Adv. Funct. Mater., 2002, 12, 245.
- 24 K. R. J. Thomas, M. Velusamy, J. T. Lin, C. H. Chuen and Y. T. Tao, *J. Mater. Chem.*, 2005, **15**, 4453.
- 25 M. Jandke, P. Strohriegl, S. Berleb, E. Werner and W. Brutting, *Macromolecules*, 1998, **31**, 6434.
- 26 K. R. J. Thomas, J. T. Lin, Y. T. Tao and C. H. Chuen, *Chem. Mater.*, 2002, 14, 2796.

- 27 G. Bernardo, M. A. Esteves, A. M. Guerreiro, B. Gigante and J. Morgado, *Opt. Mater.*, 2008, **31**, 320.
- 28 T. Hirayamaa, S. Yamasaki, H. Ameku, I. Tsutomu, T. Thiemann and S. Mataka, *Dyes Pigm.*, 2005, **67**, 105.
- 29 Y. Chandrasekaran, G. K. Dutta, R. B. Kanth and S. Patil, *Dyes Pigm.*, 2009, **83**, 162.
- 30 M. A. Reddy, A. Thomas, G. Mallesham, B. Sridhar, V. J. Rao and K. Bhanuprakash, *Tetrahedron Lett.*, 2011, 52, 6942.
- 31 K. R. J. Thomas and P. Tyagi, J. Org. Chem., 2010, 75, 8100.
- 32 A. Iyer, J. Bjorgaard, T. Anderson and M. E. Köse, *Macromolecules*, 2012, **45**, 6380.
- 33 A. M. Shaikh, B. K. Sharma and R. M. Kamble, *J. Chem. Sci.*, 2015, **127**(9), 1571.
- 34 A. M. Shaikh, B. K. Sharma, S. Chacko and R. M. Kamble, *RSC Adv.*, 2016, **6**, 60084.
- 35 S. A. VanSlyke, C. H. Chen and C. W. Tang, *Appl. Phys. Lett.*, 1996, **69**(15), 2160.
- 36 C. Adachi and K. Nagai, Appl. Phys. Lett., 1995, 66, 2679.
- 37 B. E. Koene, D. E. Loy and M. E. Thompson, *Chem. Mater.*, 1998, **10**, 2235.
- 38 C. Wu, P. I. Djurovich and M. E. Thompson, *Adv. Funct. Mater.*, 2009, **19**, 3157.
- 39 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spretizer and M. Gratzel, *Nature*, 1998, 395, 583.
- 40 U. Bach, Y. Tachibana, J.-E. Moser, S. A. Haque, J. R. Durrant, M. Gratzel and D. R. Klug, *J. Am. Chem. Soc.*, 1999, **121**, 7445.
- 41 P. G. Williard and C. Sun, J. Am. Chem. Soc., 1997, **119**(48), 11693.
- 42 Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto and T. Ohara, *J. Am. Chem. Soc.*, 2000, **122**(44), 11021.
- 43 H. Tanaka, S. Tokito, Y. Taga and A. Okada, *Chem. Commun.*, 1996, 2175.
- 44 Organic light emitting materials and devices, ed. Z. Li and H. Meng, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2007, ch. 3.

- 45 Z. Wang, X. Song, L. Ma, Y. Feng, C. Gu, X. Zhang, P. Lu and Y. Ma, *New J. Chem.*, 2013, **37**, 2440.
- 46 A. S. Guran and S. L. Buchwald, *J. Am. Chem. Soc.*, 1994, **116**, 7901.
- 47 F. Paul, J. Patt and J. F. Hartwig, *J. Am. Chem. Soc.*, 1994, **116**, 5969.
- 48 Y. Zhang, J. Y. Zou, H.-L. Yip, K.-S. Chen, D. F. Zeigler, Y. Sun and A. K.-Y. Jen, *Chem. Mater.*, 2011, **23**, 2289.
- 49 K. Brunner, A. van Dijken, H. Borner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. Langeveld, *J. Am. Chem. Soc.*, 2004, **126**, 6035.
- 50 J.-D. You, S.-R. Tseng, H.-F. Meng, F.-W. Yen, I.-F. Lin and S.-F. Horng, *Org. Electron.*, 2009, **10**, 1610.
- 51 Y. Shirota and H. Kageyama, Chem. Rev., 2007, 107(4), 953.
- 52 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, Malick, A. D. Rabuck, K. Raghavachari, D. K. J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, Al-Laham, C. Y. Peng, A. Nanayakkara, M. A. M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, 03, Revision D.02, Gaussian, Inc., Wallingford CT, 2004.
- 53 A. M. Bond, T. L. E. Henderson, D. R. Mann, W. Thormann and C. G. Zoski, *Anal. Chem.*, 1988, **60**, 1878.