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Novel electroluminescent donor-acceptors based on dibenzo[a,c]phenazine as hole-transporting materials for organic electronics[†]

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A series of novel donor-acceptor type of molecules (2–6) based on dibenzo[a,c]phenazine were synthesized by employing a palladium = catalyzed C–N bond forming amination reaction in a good yield and were then fully characterized, whereby the optical properties of 2–6 were determined by UV-vis absorption, fluorescence spectroscopy, and the electrochemical properties by cyclic voltammetry. The absorption spectra of 2–6 showed intramolecular charge transfer (ICT) transitions in the range of 447–513 nm in solution. The HOMO and LUMO energy levels of 2–6 were in the range from –5.03 to –5.29 eV and –2.75 to –2.87 eV, respectively, with an electrochemical band gap within 2.26–2.45 eV. The HOMO energy levels of 2–6 are comparable with those of the most commonly used hole-transporting materials, which makes them potential candidates for hole-transporting materials in organic electronics.

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1. Introduction

Over the last few decades, astonishing progress has been made in the field of organic electronics from industry to academics, including in organic light-emitting devices (OLEDs),¹ organic field effect transistors (OFETs),² and dye-sensitized solar cells (DSSCs).³ Small organic π -conjugated molecules with a donoracceptor (D–A) architecture have attracted significant attention due to their unique properties, such as bipolar charge (electron and hole) transport and high luminescence quantum yield,⁴ well-defined structures, ease of purification, reliable reproducibility, better solubility in most organic solvents, and easy fabrication for large area photovoltaic devices.⁵ The luminescence from such D–A systems arises from the intramolecular charge transfer (ICT) excited states or due to excimers or exciplexes formation, and further their optoelectronic properties can be tuned over a broad range by modifying the D–A moieties.⁶

In the recent past, a variety of D–A types of molecules based on anthracene,⁷ benzimidazole,⁸ carbazole,⁹ dibenzothiophene,¹⁰ fluorene,¹¹ pyrene,¹² and quinoxaline,¹³ *etc.* have been synthesized and extensively utilized as electroluminescent materials in organic electronic devices. Typically an OLED consisting of an anode (e.g., Indium tin oxide (ITO)), a hole-transporting material (HTM), a light-emitting layer, and electron-transporting material (ETM), and a metallic cathode.^{1a} The efficiency and durability of organic electronic devices depend upon the stability of both the hole- and electron-transporting materials.1a Generally HTMs should possess good hole mobility and an appropriate HOMO level and LUMO level for smooth functioning of the device. Continuous efforts are also being made with HTMs to decrease the energy barrier between the anode and emissive material and to shift the recombination area (recombination of charge carriers) toward the middle of the device to prevent quenching of the excitons (electron-hole pair) in the device¹⁴ and thus enhance the stability and lifetime of the device. So far, a number of aromatic amine derivatives have been utilized for HTMs, including α-NPD (N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,10biphenyl)-4,4'-diamine), TPD (N,N'-bis(3-methylphenyl)-N,N'diphenylbenzidine), spiro-OMe-TAD (2,2',7,7'-tetrakis[N,N-di(4methoxyphenyl)amino]-9,9'-spirobifluorene),15 Shirota star shaped molecules,16 and oligomeric amines.17

However, there is still a large scope for other organic materials to act as alternatives to the above-mentioned commonly used hole-transporting materials. In the literature, very few reports can be been found on phenazine derivatives, which include dihydrophenazine derivatives¹⁸ and polymers based on 2,7-dioctylsubstituted dibenzo[*a*,*c*]phenazine¹⁹ for solar cells. Very recently, S. Yagi *et al.*²⁰ (2015) reported 10,13-disubsitituted dipyrido[3,2*a*:2',3'-*c*]phenazine (dppz) derivatives for organic electronics. Thus, in this work, considering the importance of D–A types of molecules and hole-transporting materials in organic electronics,

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we designed and synthesized compounds 2-6 by incorporating a Buchwald-Hartwig coupling amination²¹ reaction between electron-deficient 3,6,11-tribromo-dibenzo[*a*,*c*]phenazine (1) and various electron-donating diarylamines at the 3rd, 6th, and 11th positions of 1 and studied their detailed optoelectronic and thermal properties. The design of compounds 2-6 was mainly based on the fact that the diarylamines are well-known electron donors, while compound 1 was selected as an electron-deficient backbone due to its coplanar structure formed by connecting two separated phenyl rings of phenyl-substituted quinoxaline derivatives with a single bond between the ortho positions.²² In compound **6**, we used morpholine amine to see the rigid effect of a cyclic aliphatic amine on the photo-electrochemical properties of dibenzo[a,c]phenazine.

Further, the studies also explored the effect of electrondonating and -withdrawing substituents on the diarylamine moiety on the photophysical and electrochemical properties, such as the intramolecular charge transfer transitions (ICT), the HOMO–LUMO energy levels, and the energy band gap. The structures of the synthesized molecules **2–6** are shown in Fig. 1.



Fig. 1 Molecular structure of compounds 2-6.

2. Results and discussion

Synthesis and characterization

The synthetic route for the synthesis of compounds 2-6 is shown in Scheme 1. Compound 1 (3,6,11-tribromodibenzo[a,c]phenazine) was synthesized in two steps. The first step involved the bromination of 9,10-phenanthrenedione with molecular bromine in nitrobenzene and it was done according to the reported procedure with an 86% yield and then confirmed by its melting point 288 °C (Lit. 286–287 °C).²³ The second step involved the synthesis of 1 by condensing 3,6,-dibromophenanthrene-9,10-dione and 4-bromo-2,3-diaminobenzene in glacial acetic acid with a 91% yield. Compounds 2-6 were obtained by the Buchwald-Hartwig coupling²¹ of 1 with the corresponding diarylamine (2-5) and morpholine (6) in the presence of palladium catalyst, a ligand, and a strong base in tetrahydrofuran (THF) (Scheme 1). Other solvents, such as toluene and dimethyl sulfoxide (DMSO), were also tried, but the best results were obtained in THF. Tris(dibenzylideneacetone)dipalladium $(Pd_2(dba)_3)$ was the source of the catalyst. Ligands such as 2-dicyclohexylphoshpino-2',6'-dimethoxy-biphenyl (SPhos), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XantPhos), and 1,1'-bis(diphenyl phosphino)ferrocene (DPPF) were used. Sodium tertiarybutoxide (t-BuONa) was used as a base. However, the use of a Pd₂(dba)₃/SPhos catalyst-ligand combination with the base t-BuONa significantly reduced the reaction time but with a good yield. Further, it is worth mentioning that no coupling reaction was observed when diarylamines bearing a functional group such as an 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 53–67% yields as dark orange to dark red solids soluble in common organic solvents, including dichloromethane, toluene, methanol, and cyclohexane. However, they were completely insoluble in water. The identity and purity of all the target compounds were confirmed by FT-IR, ¹H, ¹³C NMR spectroscopy, high resolution mass spectroscopy (HRMS), and elemental analysis.

Photophysical properties

The absorption and photoluminescence properties of compounds **2–6** were studied by UV-visible and fluorescence spectroscopy. In order to understand the effect of solvent polarity on the photophysical properties of **2–6**, their absorption and emission spectra were recorded in solvents of different polarity (cyclohexane, toluene, dichloromethane, methanol, and dimethyl sulfoxide) and in a neat solid film. The synthesized molecules showed similar UV-vis absorption spectra in all the above solvents and in a neat solid film (Fig. 2).

Compound **1** showed absorption maxima at 288, 384, and 406 nm in toluene, which were due to $n-\pi^*$ and $\pi-\pi^*$ transitions (see the ESI[†]). The absorption spectra of **2–6** in all the mentioned solvents showed major bands around 297–341 nm,



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

Table 1 Absorption data of compounds 2-6

	λ_{abs}^{a} , nm (log $\varepsilon_{max} M^{-1} cm^{-1}$)						
Compd	Toluene	Cyclohexane	CH_2Cl_2	CH ₃ OH	DMSO	Film	
2	308 (4.85), 339 (4.72), 496 (4.69)	307 (5.02), 338 (4.73), 491 (4.88)	307 (4.78), 341 (4.64), 491 (4.50)	303 (4.81), 339 (4.71), 494 (4.64)	307 (4.82), 339 (4.75), 503 (4.69)	340, 510	
3 4	322 (4.85), 490 (4.76) 308 (4.85), 507 (4.48)	322 (5.04), 484 (5.01), 307 (5.02), 502 (4.56)	329 (4.74), 493 (4.63) 310 (4.77), 508 (4.52)	323 (4.79), 491 (4.78) 308 (4.57), 508 (4.41)	329 (4.99), 499 (4.87) 329 (4.60), 513 (4.45)	334, 497 341, 517	
5	317 (4.91), 508 (4.96)	311 (4.94), 501 (5.01),	316 (4.91), 510 (4.98)	311 (3.89), 503 (3.98)	316 (4.90), 512 (4.93)	313, 439 514	
6	299 (4.98), 457 (4.70)	300 (4.89), 447 (4.59)	297 (4.95), 458 (4.68)	297 (4.62), 456 (4.37)	307 (4.92), 472 (4.68)	300, 468	
^{<i>a</i>} Recorded in 10^{-5} M solution.							

corresponding to $n-\pi^*$ and $\pi-\pi^*$ transitions. This high energy transition originated from the entire dibenzo[*a*,*c*]phenazine skeleton. Apart from the $n-\pi^*$ and $\pi-\pi^*$ transitions, the synthesized compounds also showed a lower energy intramolecular charge transfer transition (ICT) around 447–513 nm (Table 1) from the various electron-donor arylamines in **2–5** and morpholine in **6** to the electron-acceptor dibenzo[*a*,*c*]phenazine segment (Fig. 2). This lowest-energy absorption band is the most sensitive to the solvent polarity and to the donor moiety (arylamines).

However no significant change was observed on increasing the solvent polarity on the $n-\pi^*$, $\pi-\pi^*$ transition, and ICT transitions in compounds **2–6**, indicating that the ground state of the molecules are more stable than the excited state. Further, a slight bathochromic shift in the ICT transition of around 9–17 nm was observed in the case of compounds **4** and **5** due to the presence of polar groups, such as methoxy (–OCH₃) and diazene, respectively, on the diarylamine moiety.

In compound **6**, a blue shift of around 31–49 nm was observed in the ICT transition and the intensities of the $n-\pi^*$,



Fig. 3 Emission spectra of 2 in various solvents (a) and in a neat solid film of 2-6 (b) (for other solvents, see ESI†).

 π - π *, and ICT transitions were found to be weak compared to other derivatives due to the presence of aliphatic cyclic amine and morpholine. The absorption of **2–6** in a neat solid film was observed in the range of 300–341 and 468–517 nm. The red

Table 2 $\,$ Emission data, Stokes shift, optical band gap, and quantum yield of compounds ${\bf 2-6}$

	$\lambda_{\rm emi}{}^a$, nm			Stokes shift ^b			
Compd	Toluene	Cyclohexane	Film	cm^{-1}	$E_{\mathrm{g}}^{\mathrm{opt}c}\left(\mathrm{eV}\right)$	$\phi_{\mathrm{F}}{}^{d}$	
2	532	510	562	13 670	2.37, (2.38)	0.41	
3	525	508	555	12 008	2.33, (2.34)	0.36	
4	583	540	609	15255	2.20, (2.21)	0.30	
5	—	_	—	—		—	
6	520	493	545	14 326	2.46, (2.48)	0.52	

^{*a*} Recorded in 10⁻⁵ M solution. ^{*b*} Recorded in 10⁻⁵ M toluene. ^{*c*} Optical band gap estimated using the emission and excitation spectra in a neat solid film 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.

shift observed in the thin film absorption maxima and slight broadening of the peak suggests the presence of intermolecular aggregation in the solid state.

All the compounds 2-6 emit in the yellow-green region on excitation at the λ_{max} obtained in the absorption spectra with the emission maxima in the range of 520-583 nm in toluene, except for compound 5. A significant red shift of around 64–154 nm was observed for 2–6 as compared to 1 (λ_{emi} = 429 nm) (see the ESI[†]) in solution. Further, a bathochromic shift of 50-62 nm was observed in compound 4 as compared to the other derivatives in toluene due to the presence of an electron-donating methoxy (-OCH₃) on the diarylamine moiety. No emission was observed in all of the solvents and in the neat solid film for compound 5 due to the presence of an electronwithdrawing diazene group on the diarylamine moiety, thus showing the influence of peripheral amines on the emission intensity. A blue shift of around 13-41 nm was observed in cyclohexane for 2-6 as compared to toluene. On increasing the polarity of the solvent from toluene to CH₂Cl₂ and DMSO, compounds 2, 3, and 6 emitted with a red shift of around



Fig. 4 Tapping mode AFM topographical images (3D) of compounds 2 and 3 neat solid film coated (1000 rpm) from chloroform solution on quartz coverslips.



Fig. 5 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 compounds 2–6

Compd	$E_{\mathrm{ox}}^{\mathrm{peak}a}$	Ered b	HOMO ^c	LUMO ^d	$E_{\mathrm{g}}^{\mathrm{EC}e}$	$T_{\rm m}^{\ f}$ (°C)	$T_{d}^{g}(^{\circ}C)$
2 3 4 5	0.95, 1.18, 1.35 0.94, 1.18, 1.39 0.72, 0.93, 1.47 1.01, 1.30, 1.64 0.87, 1.02, 1.23	-1.64 -1.59 -1.69 -1.59 -1.71	-5.23 -5.23 -5.03 -5.29 -5.15	-2.78 -2.85 -2.77 -2.87 -2.75	2.45 2.38 2.26 2.42 2.40	272 238 240 262 223	330 (495) 291 (481) 280 (350) 366 (399) 270 (340)

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

18–55 nm, thus showing positive solvatochromism. However, quenching in the emission was observed for **2–6** in methanol, while compounds **4** and **5** did not emit in CH_2Cl_2 and DMSO, suggesting a nonradiative relaxation from the excited state to

the ground state in polar solvents due to the presence of polar groups, such as $-OCH_3$ and diazene.

A red shift of around 25-30 nm was observed in the neat solid film as compared to in toluene (Fig. 3(b)), which may be due to intermolecular aggregation in the solid state. The optical band gaps of 2-6 were determined by the intersection of the emission and excitation spectra. A large Stokes shift was observed for 2-6, which suggest a considerable change in the ground and excited state geometry (Table 2). The quantum yields of 2–6 were calculated using fluorescein ($\phi = 0.79$ in ethanol) as a reference. The quantum yields were found to be high and to depend on the electron-donating nature of diarylamines at the 3rd, 6th, and 11th positions of the dibenzo[a,c]phenazine backbone. The morphological characteristics of the neat solid film of compounds 2-6 were studied by atomic force microscopy (AFM) in the tapping mode. Fig. 4 shows the AFM results of compounds 2 and 3, while for other compounds, see ESI.† The AFM results show a smooth film with



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

a root mean square (rms) roughness value of 0.94–8.72 nm, while micrometer-sized phase separation was not observed.

Electrochemical properties

The redox properties and molecular orbital energy levels (HOMO and LUMO) of compounds **2–6** were studied by cyclic voltammetry (CV) (Fig. 5) in anhydrous dichloromethane solution using ferrocene as an internal standard to calibrate the redox potentials, and the pertinent data is presented in Table 3.

On an anodic sweep, three quasi-reversible waves were observed for all compounds 2-6, which was attributed to the oxidation of the diarylamine moiety at the 3rd, 6th, and 11th positions of the dibenzo[a,c]phenazine moiety, suggesting three electrons were removed successfully from three nitrogen atoms. The E_{oxi} potential of 2-6 decreased on increasing the donor strength (4 > 6 > 3 > 2 > 5). On a cathodic sweep, one reversible wave was observed for 2-6 (see the ESI⁺), corresponding to reduction of the dibenzo [a, c] phenazine core. The energy levels of the highest occupied and lowest orbitals included TPD (HOMO = -5.12 eV,^{15b} α -NPD (HOMO = -5.20 eV),^{1a,15a} spiro-OMe-TAD (HOMO = -5.22 eV),^{15c-f} DMFL-NPB (9,9-dimethyl-N,N'-di- $(1-naphthyl)-N,N'-diphenyl-9H-fluorene-2,7-diamine)^{24}$ (HOMO = -5.20 eV), 1,3,5-tris(2-(9-ethylcabazyl-3)ethylene)benzene (HOMO = -5.20 eV).²⁵ Thus, with a lower HOMO energy level, compounds 2-6 may act as hole-transporting materials. Unoccupied molecular orbital's (HOMO and LUMO) were calculated from the first oxidation and reduction potentials. The HOMO and LUMO energy levels of 2-6 were found to be in the

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

Compd	EA (eV)	IP (eV)	HOMO (eV)	LUMO (eV)	$E_{\rm g}^{\rm TH}$	$\mu_{\rm g}$ (debye)
2	1.13	5.94	-5.06	-2.23	2.82	0.88
3	1.06	5.90	-5.04	-2.11	2.93	1.30
4	0.91	5.58	-4.74	-1.98	2.75	0.89
5	1.81	6.02	-5.27	-2.58	2.69	3.11
6	0.84	6.25	-5.14	-2.08	3.06	0.22

range of -5.03 to -5.29 eV and -2.75 to -2.87 eV, respectively. The HOMO energy levels of **2–6** are comparable to those of the commonly used/reported hole-transporting materials.

The energy band gap calculated from the cyclic voltammetry measurements were in the range of 2.26–2.45 eV and closely matched with the optical band gap. A decrease in band gap was observed in compound 4 (2.26 eV), indicating the influence of the electron-donating $-OCH_3$ group on the diarylamine moiety at the 3rd, 6th, and 11th positions of the dibenzo[a,c]phenazine moiety (Table 3). Thus, the presence of an electron-donating substituent on the diarylamine moiety results in a decrease in the HOMO and LUMO energy levels and the energy band gap.

Theoretical properties

In order to understand the molecular orbital levels and electrical properties of compounds **2–6** theoretically, 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.²⁶ Fig. 6 show the theoretically calculated molecular orbitals of **2–6**. The theoretically calculated HOMO and LUMO of **2–6** were in the range of -4.74 to -5.27 eV and -1.98 to -2.58 eV, respectively, and were in close agreement with those calculated by CV (Table 4). The HOMO energy levels of **2–6** were found to be localized throughout the molecule (Fig. 6), indicating that the HOMO energy levels were contributed by both the electron-donating/acceptor moieties, while the LUMO energy levels of **2–6** were mainly located on the dibenzo[*a*,*c*]phenazine backbone.

Thus, HOMO–LUMO transitions occur from the electrondonor diarylamines to the electron-acceptor dibenzo[a,c]phenazine backbone. The first ionization potential, the electron affinity, the energies of the HOMO and LUMO levels, the HOMO–LUMO gap, and the ground-state dipole moment computed for **2–6** are listed in Table 4. The dipole moment calculated for **2–6** were found to be low as the dipole vectors lie in opposite directions and cancel each other out, whereas the dipole moment of **4** (3.11) was high, compared to the other compounds, due to the presence of an electron-withdrawing diazene group on the diarylamine moiety.



Fig. 7 (a) TGA and (b) DSC thermograms of compounds 2-6 under a nitrogen atmosphere at normal pressure. Heating rate, 10 °C min⁻¹.

Thermal properties

The thermal investigations of compounds **2–6** were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The melting points of **2–6** were determined by DSC (Fig. 7b) and were in the range of 223–272 °C.

No glass phase transitions were observed in all the compounds 2–6 (see the ESI†). The TGA thermograms (Fig. 7(a)) of compounds 2–6 revealed that these derivatives had 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 270–366 °C and 340–495 °C, respectively (Table 3). The order of thermal stability among the synthesized derivatives was 5 > 2 > 3 > 4 > 6. The high thermal stability of **2–6** makes them suitable for device fabrication and to facilitate an enhanced lifetime of the devices.

3. Conclusions

A series of 3,6,11-trisubstituted-dibenzo[*a*,*c*]phenazine derivatives were synthesized via a Buchwald-Hartwig palladium-catalyzed C-N bond forming reaction using a Pd₂(dba)₃/SPhos catalyst system in good yields. The absorption, electrochemical, and thermal properties of the synthesized materials were significantly influenced by the nature of the peripheral amine segment attached to the dibenzo[a,c] phenazine core. Compounds 2–6 emitted in the green region (545-609 nm) in a neat solid film, except for compound 5. The ionization potentials (HOMO energy levels) of 2-6 were found in the range of -5.03 to -5.29 eV and were comparable to those of the commonly used/reported hole-transporting materials. The theoretically obtained results were found to be consistent with the experimental results. The thermal properties revealed that the derivatives had high melting points and good thermal stability. Thus, on the basis of the experimental and theoretical results, we believe that these compounds have the potential to be used as hole-transporting materials in optoelectronic devices.

4. Experimental section

Chemicals and materials

All the starting materials and reagents were purchased from commercial sources (Sigma Aldrich and Alfa Aesar) and were used without any further treatment and purification 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 a 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 the 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 an iodine chamber.

Instrumentation and methods

UV-visible spectra were recorded in 10^{-5} mol L⁻¹ solutions in a 1 cm path length quartz cuvette as were the neat solid films on

a SHIMADZU UV-2401PC instrument at room temperature. The neat solid films of compounds 2-6 were prepared by using a spin coater (Holmarc HO-TH-05) at 1000 rpm for 2 min using $\sim 6 \text{ mg ml}^{-1}$ of sample in chloroform. Quartz coverslips were used for the neat solid film studies. The AFM topographical images were recorded on a Bruker Dimension Icon AFM instrument. The excitation and emission spectra were carried out on a Perkin Elmer LS 55 Fluorescence spectrophotometer. The 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. Typically, a three electrode cell equipped with a glassy carbon working electrode, a Ag/AgCl (non-aqueous) reference electrode, and platinum (Pt) wire as the counter electrode was employed. The measurements were carried at room temperature in anhydrous acetonitrile with tetra butyl ammonium hexafluorophosphate solution (0.1 M) as the supporting electrolyte with a scan rate of 100 mV s⁻¹. The potential of the Ag/AgCl reference electrode was calibrated by using a ferrocene/ferrocenium redox couple, which has the known oxidation potential of +4.8 eV.²⁷ The melting point of the products were determined by differential scanning calorimetry (DSC). The thermogravimetric analysis (TGA) and DSC were performed using a Metler Toledo instrument (TG/DSC) under a nitrogen atmosphere. ¹H NMR spectra and ¹³C NMR spectra were recorded using CDCl₃ on a Bruker 300 Ultrashield spectrometer with tetramethylsilane (TMS) as the 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 a Maxis Impact 282001.00081 instrument using Bruker Compass data analysis 4.1, while elemental analysis was carried on an EA Euro-elemental analysis instrument.

Synthetic procedures

Synthesis of 3,6,11-tribromodibenzo[*a*,*c*]phenazine (1). A mixture of 3,6,-dibromophenanthrene-9,10-dione (0.92 g, 2.5 mmol) and 4-bromo-2,3-diaminobenzene (0.47 g, 2.5 mmol) was dissolved in 25 ml of glacial acetic acid and refluxed for 5 h. The reaction mixture was allowed to cool and then poured over crushed ice to obtain a light green colored solid. The obtained solid was then dried under vacuum and purified using column chromatography (eluent: *n*-hexane: chloroform ratio as 60:40) to obtain a light green solid. Yield: 1.17 g (91%), mp: > 360 °C. FT-IR (KBr, $\nu_{\rm max}~{\rm cm}^{-1}$): 3055.89, 1589.09, 1285.89, 1045.15, 824.23, 723.56; ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.09 (d, J = 9.3 Hz, 1H), 7.77 (d, J = 1.8 Hz, 2H), 7.54 (d, J = 2.7 Hz, 1H), 7.51(d, J = 2.7 Hz, 1H), 7.43 (d, J = 2.7 Hz, 1H), 7.32 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 7.26 (s, 1H); ¹³C NMR (75 MHz, $CDCl_3$: δ (ppm) = 152.49, 152.13, 151.39, 143.26, 142.26, 139.96, 137.73, 133.19, 132.37, 129.63, 127.54, 127.03, 123.80, 123.38, 121.75, 116.78, 116.49, 109.23, 107.32, 107.16; MS: C₂₀H₉Br₃N₂, m/z: 518.87 [M + 1]⁺; elemental anal. calcd for C₂₀H₉Br₃N₂: C 46.46, H 1.75, Br 46.36, N5.42. found: C 46.40, H 1.74, Br 46.39, N 5.46.

General procedure for the synthesis of compounds 2–6. A mixture of compound 1 (0.122 g, 0.25 mmol) and various diarylamines (0.6 mmol) was dissolved in anhydrous tetra-hydrofuran (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 a nitrogen atmosphere at 80 °C for 6 h. The 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) to obtain a dark red to dark orange solid.

 $N^3, N^6, N^6, N^{11}, N^{11}$ -Hexaphenyldibenzo[a,c]phenazine-3,6,11triamine (2). Dark orange solid, yield: 129 mg (66%), mp: 272 °C. FT-IR (KBr, ν_{max} cm⁻¹): 3033.43, 1585.98, 1485.72, 748.39, 691.76; ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.06 (d, J =9.0 Hz, 1H), 8.99 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.62–7.63 (m, 3H), 7.55 (d, J = 9.0 Hz, 2H), 7.38–7.03 (m, 31H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 149.60, 149.31, 149.21, 147.98, 147.09, 147.07, 146.97, 143.18, 142.34, 142.28, 140.34, 138.83, 132.88, 132.24, 129.59, 129.40, 127.15, 125.58, 124.48, 124.21, 123.89, 123.79, 122.51, 122.19, 117.09, 115.59, 114.87, 114.62; HRMS: calcd for C₅₆H₄₀N₅ [M + H]⁺; 782.3278 found 782.3293; elemental anal. calcd for C₅₆H₃₉N₅: C 86.02, H 5.03, N 8.96. found: C 86.12, H 4.93, N 8.95.

 N^3 , N^6 , N^{11} -*Tri(naphthlen-1-yl)*- N^6 , N^{11} -*triphenyldibenzo[a,c]-phenazine-3,6,11-triamine (3).* Red solid, yield: 139 mg (60%), mp: 238 °C. FT-IR (KBr, ν_{max} cm⁻¹): 3055.03, 1590.24, 1488.12, 1357.10, 770.23, 693.04; ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.00 (d, J = 9.0 Hz, 1H), 8.97 (d, J = 9.0 Hz, 1H), 7.96–7.73 (m, 10H), 7.51–6.97 (m, 33H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 150.06, 149.65, 149.06, 147.45, 147.38, 147.26, 145.42, 143.17, 142.82, 142.71, 142.61, 142.26, 140.15, 138.43, 135.40, 135.16, 132.91, 132.20, 131.13, 131.08, 131.01, 129.42, 129.18, 128.51, 128.42, 127.56, 127.33, 127.21, 127.03, 126.99, 126.72, 126.53, 126.38, 126.30, 126.14, 125.23, 124.30, 123.97, 123.56, 123.41, 123.11, 123.04, 122.97, 122.90, 120.90, 120.60, 115.07, 112.75; HRMS: calcd for C₆₈H₄₆N₅ [M + H]⁺ 932.3646; found 932.3781; elemental anal. calcd for C₆₈H₄₅N₅: C 87.62, H 4.87, N 7.51. found: C 87.52, H 4.97, N 7.52.

 $N^3, N^3, N^6, N^6, N^{11}, N^{11}$ -Hexakis(4-methoxyphenyl)dibenzo[a, c]phenazine-3, 6, 11-triamine (4). Dark red solid, yield: 161 mg (67%), mp: 240 °C. FT-IR (KBr, ν_{max} cm⁻¹): 3037.72, 3000.07, 2928.33, 1598.68, 1502.71, 1236.60, 1030.52, 824.80; ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.96 (d, J = 9.0 Hz, 1H), 8.91 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 3.9 Hz, 1H), 7.91 (d, J = 3.9 Hz, 1H), 7.51 (s, 3H), 7.45 (d, J = 2.7Hz, 2H), 7.17 (d, J = 9.0 Hz, 6H), 7.06 (d, J = 9.0 Hz, 6H), 6.88 (d, J = 9.0 Hz, 6H), 6.80 (d, J = 9.0 Hz, 6H), 3.81 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 156.66, 156.36, 156.27, 150.20, 149.74, 149.21, 142.38, 140.25, 140.21, 140.10, 139.92, 132.93, 132.14, 129.12, 127.38, 127.13, 127.00, 126.89, 126.47, 124.77, 123.27, 120.34, 119.93, 114.97, 114.72, 113.63, 112.15, 111.82, 55.51, 55.40; HRMS: calcd for C₆₂H₅₂N₅O₆ [M + H]⁺ 962.3912; found 962.3932; elemental anal. calcd for $C_{62}H_{51}N_5O_6{:}\ C$ 77.40, H 5.34, N 7.28, O, 9.98. found: C 77.42, H 5.33, N 7.19, O 10.06.

 N^3 , N^6 , N^{11} -Triphenyl- N^6 , N^{11} , N^{11} -tris(4-(E)-(phenyldiazenyl)phenyl)dibenzo[a,c]phenazine-3,6,11-triamine (5). Dark red solid, vield: 145 mg (53%), mp: 262 °C. FT-IR (KBr, ν_{max} cm⁻¹): 3035.43, 1586.07, 1488.55, 1269.42, 686.22; ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 9.12 (d, J = 9.0 Hz, 1H), 9.04 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 2H), 7.90–7.74 (m, 14H), 7.63 (d, J = 2.7 Hz, 1H), 7.60 (d, J = 2.7 Hz, 2H), 7.51–7.15 (m, 30H); ¹³C NMR (75 MHz, $CDCl_3$): δ (ppm) = 156.30, 152.89, 149.66, 148.93, 148.58, 148.41, 147.98, 147.90, 146.46, 146.34, 146.28, 143.15, 142.28, 141.95, 140.67, 139.42, 133.35, 132.85, 132.32, 131.88, 130.43, 129.91, 129.71, 129.05, 127.50, 127.38, 127.15, 126.39, 126.21, 125.80, 125.48, 125.23, 125.07, 124.40, 124.31, 123.75, 123.25, 123.14, 122.67, 122.62, 119.34, 116.48, 116.29, 116.28; HRMS: calcd for C75H52N11 $[M + H]^+$ 1094.4323; found 1094.4411; elemental anal. calcd for C75H51N11: C 81.22, H 4.70, N 14.08. found: C 81.32, H 4.63, N 14.05.

4,4',4"-(Dibenzo[a,c]phenazine-3,6,11-triyl)trimorpholine (6). Orange solid, yield: 82 mg (61%), mp: 223 °C. FT-IR (KBr, $\nu_{\rm max}$ cm⁻¹): 3479.23, 2920.34, 2848.93, 1604.23, 1362.36, 1106.52, 685.90; ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.09 (d, *J* = 9.0 Hz, 1H), 7.79 (s, 2H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 1H), 3.97 (t, *J* = 4.5 Hz, 12H), 3.42 (t, *J* = 4.5 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 152.48, 152.15, 151.23, 143.49, 142.19, 140.01, 132.40, 132.31, 129.65, 127.21, 121.88, 121.57, 116.51, 116.35, 116.20, 109.38, 108.93, 108.28, 107.19, 107.03, 66.92, 66.81, 49.41, 49.14; HRMS: calcd for C₃₂H₃₄N₅O₃ [M + H]⁺ 536.2656; found 536.2650; elemental anal. calcd for C₃₂H₃₃N₅O₃: C 71.75, H 6.21, N 13.07, O, 8.96. found: C 71.70, H 6.23, N 13.19, O 8.98.

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