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Novel multiresonant diindolophenazine fluorophore as a hole-transport organic semiconductor

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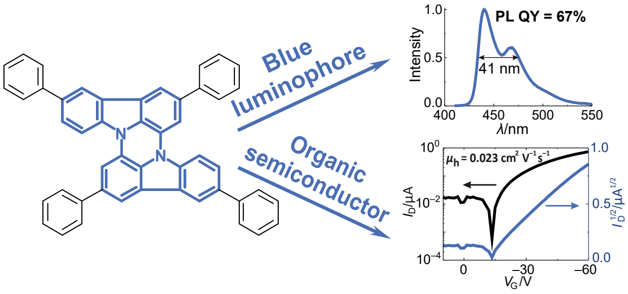
A novel multiresonant fluorophore 2,5,10,13-tetraphenyl-diindolo[3,2,1-*de*:3′,2′,1′-*kl*]phenazine was investigated computationally using (TD)DFT, synthesized and characterized; it emits blue light with a photoluminescence maximum at 436 nm and a quantum yield of 67%. Organic field-effect transistors based on this compound as an organic semiconductor showed a significant hole mobility of up to 0.023 cm^2 V^{-1} s^{-1}, highlighting the potential of multiresonant fluorophores as multifunctional compounds that can be used in both charge-transporting and light-emitting layers of organic (opto)electronic devices.



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Organic electronics is a rapidly growing area of science and technology aimed at producing next-generation electronic devices based on organic semiconductors.[1–3] Organic optoelectronics is certainly one of the most successful branches of organic electronics.[4,5] Specifically, organic light-emitting diodes (OLEDs) are actively used in mobile phone and TV displays.[1,6] Photophysics and charge transport in organic semiconductors, which are the keystones for organic electronic devices, are addressed in a number of books and reviews.[4,6–8]

Multiresonant organic fluorophores are among the most promising novel compounds for emissive layers of OLEDs.[1,9–15] Their annulated polycyclic aromatic cores with heteroatoms such as N, B and sometimes O or S induce the so-called 'multiple resonance' effect, *i.e.*, a combination of opposite resonance effects of substituents.[14,15] As a result, the frontier molecular orbitals, namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), acquire maximum density near the atoms due to a decrease in the density on the bonds, becoming, as a consequence, non-bonding. Meanwhile, the centers of mass of the frontier orbital densities are very close.[10,14,15] Such a pattern of the HOMO and LUMO reduces the electron–vibrational coupling and, therefore, narrows the emission spectrum (down to 10 nm),[1,9–13] ensuring the color purity required for displays. Popular multiresonant organic fluorophores include N- and B-containing compounds such as diazaboranaphthoantracenes,[10,14] indolocarbazoles[11] and diindolophenazines.[12]

Weak electron–vibrational coupling in multiresonant organic fluorophores should favor high charge carrier mobility.[7] Indeed, according to the widely used hopping model of charge transport based on the Marcus formula for the charge transfer rate,[16,17] the charge carrier mobility decreases exponentially with increasing reorganization energy λ, an integral characteristic of electron–vibrational coupling. However, charge transport in materials based on multiresonant organic fluorophores has not been studied so far. In this work, we synthesize a novel multiresonant organic fluorophore 2,5,10,13-tetraphenyl-diindolo[3,2,1-*de*:3′,2′,1′-*kl*]phenazine (PhDIPz) and investigate it both experimentally and theoretically[†] as a promising fluorophore and hole-transport organic semiconductor.

Figure 1 shows the atomic positions in optimized equilibrium geometries of PhDIPz, along with the HOMO, LUMO and natural transition orbitals (HOTO/LUTO) corresponding to the $S_1 \rightarrow S_0$ transition in this molecule. The annulated core is planar, and the dihedral angles between any four atoms in the neutral, anionic or cationic forms are less than 3°. Notably, the natural orbitals reveal that in the diindolophenazine core, the HOTO density is highest near individual atoms and is low at chemical bonds. LUTO shows a similar pattern, but with density maxima

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[†] To predict the properties of PhDIPz, quantum chemical calculations were performed using density functional theory (DFT) and time-dependent DFT (TDDFT). The geometries of the ground state (S_0), the first excited singlet state (S_1), as well as the anionic and cationic forms of the ground state were optimized using the B3LYP exchange-correlation functional,[18] the def2-SVP basis set[19] and the D3BJ dispersion correction.[20] To improve the accuracy of energy determination, single-point calculations (including TDDFT) were performed with the def2-TZVP basis set[21] using the optimized geometries mentioned above. The chosen computational approach has previously demonstrated good agreement with experimental data for indolocarbazole-based multiresonant fluorophores.[12] All computations were carried out using the ORCA software package.[22]

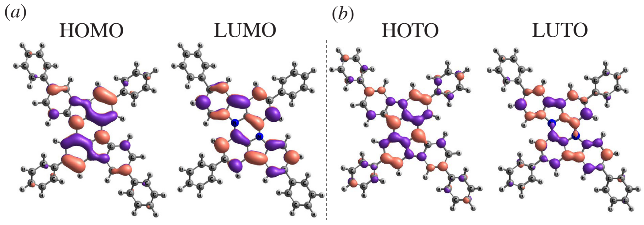
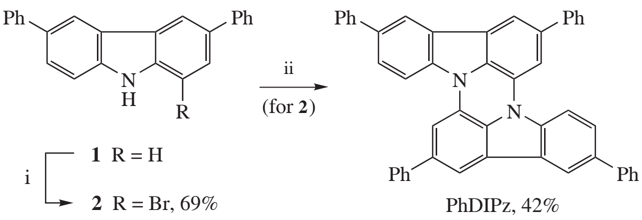


Figure 1 (*a*) Patterns of frontier molecular orbitals and (*b*) patterns of natural transition orbitals corresponding to the $S_1 \rightarrow S_0$ transition in the studied PhDIPz molecule.

near a different set of atoms, confirming the multiresonance effect.[10] The calculated HOMO and LUMO energies are –4.98 and –1.54 eV, respectively. The LUMO energy is relatively high compared to those of popular organic semiconductors exhibiting decent electronic conductivity, such as naphthalene/perylene diimides or TCNQ derivatives, which typically have LUMO energy below –3 eV.[23,24] The advantage of such a low LUMO energy for electron transport is dictated by the conditions for electron injection from standard electrodes, such as Ca/CsF,[25] which would otherwise be poor. On the contrary, the high HOMO energy is comparable to that of the best hole-conducting organic semiconductors and implies efficient hole injection. Moreover, such HOMO energy is consistent with trap-free charge transport, in contrast to the LUMO energy, which should be below –4 eV.[26] For these reasons, testing of PhDIPz as a hole-transporting organic semiconductor is feasible. The ionization potential of PhDIPz was found to be 5.99 eV, and the electron affinity was 0.53 eV. The HOMO–LUMO energy gap was calculated to be 3.44 eV, while the optical gap (energy of the $S_0 \rightarrow S_1$ transition, corresponding to absorption) was 2.9 eV. The energy of the $S_1 \rightarrow S_0$ transition (corresponding to emission and being lower than the energy of $S_0 \rightarrow S_1$ due to relaxation of the S_1 state) was estimated to be 2.77 eV (448 nm), which suggests blue emission of PhDIPz and predicts a small Stokes shift. The oscillator strength of this transition was calculated to be 0.339, which is consistent with the values reported for diindolophenazines[12] and indolocarbazoles.[13]

The reorganization energies for holes and electrons were defined as $\lambda = (E_{IN} - E_{II}) + (E_{NI} - E_{NN})$, where E_{IN} is the energy of the ion (cation for holes, anion for electrons) in the neutral geometry, E_{II} is the energy of the ion in the equilibrium geometry, E_{NI} is the energy of the neutral state in the ionic geometry, and E_{NN} is the energy of the neutral state in the neutral geometry. The calculated reorganization energies are as small as 121 meV for holes and 164 meV for electrons, which are comparable to those of tetracene and rubrene, for which charge mobilities exceeding 1 $cm^2\ V^{-1}\ s^{-1}$ have been reported.[4,27] The small hole/electron reorganization energies indicate weak electron–phonon coupling, which can be attributed to the low HOMO/LUMO density on the bonds and significant charge delocalization [Figure 1(*a*)]. Indeed, for these reasons, the bond length changes resulting from hole/electron acquisition (and during vibrations) have little effect on the HOMO/LUMO energies, *i.e.* even if the geometry relaxation is strong, it does not translate into strong energy relaxation, and hence both $(E_{IN} - E_{II})$ and $(E_{NI} - E_{NN})$ are small.[8] The second main factor determining the charge mobility in the hopping model incorporating the Marcus formula for the hopping rate,[16,17] namely the transfer integrals J, were also assessed. For this purpose, the structure of the amorphous PhDiPz film was simulated using molecular dynamics,[‡] pairs of adjacent molecules were detected, and then the J values were calculated using the DIPRO approach.[28] The obtained J values were rather high and reached 68 meV, suggesting sufficient charge carrier mobility. Given the high HOMO and LUMO energies compared to popular organic semiconductors[23,24] and the 'trap-free window'[26] (see above), PhDIPz-based organic semiconductors should exhibit efficient hole transport in organic field-effect transistors (OFETs).

The synthetic route of PhDIPz is presented in Scheme 1. 3,6-Diphenyl-9*H*-carbazole **1** was synthesized as described previously.[29] Reaction of this compound with one equivalent of *N*-bromosuccinimide (NBS) afforded 1-bromo-3,6-diphenyl-9*H*-carbazole **2** in 69% yield. Finally, compound **2** was dimerized to form PhDIPz under Ullmann reaction conditions. The yield of the final product after purification was 42%.[‡]



Scheme 1 *Reagents and conditions*: i, NBS, DMF; ii, 18-crown-6, CuI, K_2CO_3, *o*-DCB.

The photoluminescence (PL) of PhDIPz was studied in diluted (~0.1 wt%) solid solutions in Paraloid.[‡] The PL excitation and emission spectra of PhDIPz [Figure 2(*a*)] are practically mirrored. The Stokes shift is very small (5 nm), which could be explained by the rigidity of the polycyclic conjugated hydrocarbon core. PL was observed in the blue region with a maximum at 436 nm, which correlates well with the theoretically calculated value (see above). Blue emission is an advantage because the basic polycyclic cores of multiresonant fluorophores usually have a large π-conjugated system emitting in the blue-green region of the spectrum. Both spectra demonstrate a pronounced vibrational structure consisting of two peaks, and the difference in their energies corresponds to the vibrational frequency of 1360 cm^{-1}, which is in the region of typical collective vibrations of the π-conjugated system in organic semiconductors.[30–35] The FWHM of the spectra is 41 nm, and the PL quantum yield reaches 67%.

The kinetic curve of PL (fluorescence) decay [Figure 2(*b*)] is monoexponential with a PL lifetime of 3.5 ns. The rate constant of the radiative process and the sum of the rate constants of nonradiative processes, including intersystem crossing and internal conversion, were found to be $k_r = 1.9 \times 10^8\ s^{-1}$ and $k_{nr} = 9.4 \times 10^7\ s^{-1}$, respectively. The experimental value of the radiative constant correlates well with that obtained in the quantum chemical modeling ($k_r = 1.2 \times 10^8\ s^{-1}$).

Finally, OFET samples were fabricated based on PhDIPz thin films prepared by thermal vacuum evaporation[‡] and used to observe hole transport. Figure 3 shows typical transfer and output characteristics of such OFETs. The charge carrier mobility and threshold voltage were determined by fitting the transfer characteristics with the Shockley equations in the linear and saturation modes.[‡] The maximum hole mobility was 0.023 $cm^2\ V^{-1}\ s^{-1}$, the average value ($n = 7$) was 0.0136 ± 0.0003 $cm^2\ V^{-1}\ s^{-1}$, and the average threshold voltage was –7 ± 3 V. The mobility values are quite high compared to those typical for thermally evaporated

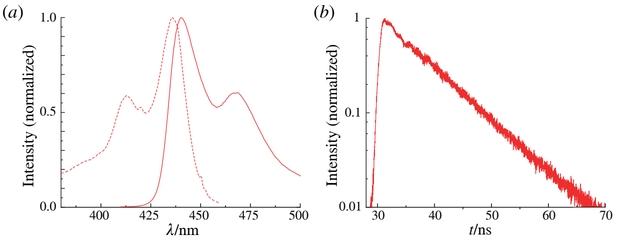


Figure 2 (*a*) PL excitation (dashed line) and emission (solid line) spectra and (*b*) PL decay kinetics for PhDIPz solid solution in Paraloid.

[‡] For details, see Online Supplementary Materials.

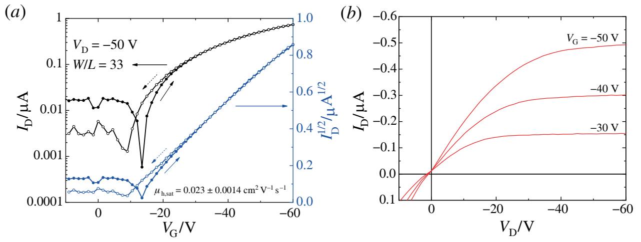


Figure 3 (*a*) Transfer and (*b*) output curves for PhDIPz-based OFETs.

organic semiconductor films.[36,37] This is consistent with the low values of the reorganization energy for hole transport (see above). Low threshold voltages indicate efficient hole injection, which is consistent with the high HOMO value. It should also be noted that the hysteresis in the transfer characteristics is very small, which indicates increased stability during electric current flow for PhDIPz thin films and a low content of impurities in it, which can act as long-lived traps for charge carriers.

In conclusion, starting from (TD)DFT calculations, we designed, synthesized and experimentally characterized a novel multiresonant fluorophore, PhDIPz. It exhibits a rather narrow PL spectrum (FWHM of 41 nm) in the blue region with a maximum at 436 nm, a clear vibrational structure and a high PL quantum yield of 67%, which makes it promising for OLED applications. Moreover, OFETs based on this compound demonstrate hole transport with a decent charge carrier mobility of up to 0.023 cm^2 V^{-1} s^{-1}, a low threshold voltage and a small hysteresis. Thus, PhDIPz can be used not only as a dopant in the emitting layers of blue OLEDs, but also as a hole-transport organic semiconductor. For example, this allows an emitting layer to be applied to a PhDIPz film as a hole-transport layer by co-deposition of PhDIPz in a matrix of another organic semiconductor. Thus, the use of the presented multifunctional compound can simplify the manufacture of organic optoelectronic devices.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7779.

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