

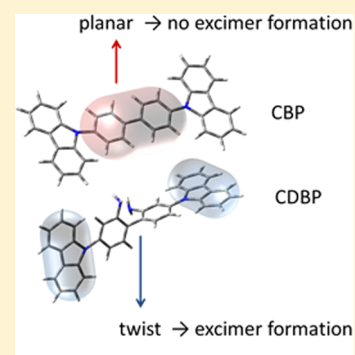


Excimer Formation by Steric Twisting in Carbazole and Triphenylamine-Based Host Materials

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Supporting Information

ABSTRACT: This paper presents a detailed spectroscopic investigation of luminescence properties of 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) and *N,N,N',N'*-tetraphenylbenzidine (TAD) in solutions and neat films. These compounds are compared to their derivatives CDBP and TDAD that contain methyl groups in the 2 and 2' position of the biphenyl core. We find that whereas steric twisting in CDBP and TDAD leads to a high triplet energy of about 3.0 and 3.1 eV, respectively, these compounds also tend to form triplet excimers in a neat film, in contrast to CBP and TAD. By comparison with *N*-phenylcarbazole (NPC) and triphenylamine (TPA), on which these compounds are based, as well as with the rigid spiro analogues to CBP and TAD we show that the reduced excimer formation in CBP and TAD can be attributed to a localization of the excitation onto the central biphenyl part of the molecule.



I. INTRODUCTION

The fabrication of organic light-emitting diodes (OLEDs) based on phosphorescence requires host materials with a triplet T_1 energy that is higher than that of the emitting phosphorescent dye. At the same time, the electron affinity needs to be high and the ionization potential low to facilitate charge injection. This implies a suitable singlet S_1 energy, and, in particular, a small S_1-T_1 energy gap.^{1,2} These requirements are relatively easy to fulfill for hosts for red and green phosphors but difficult for blue phosphors with triplet energies up to about 2.8 eV. Examples of hosts suitable for green emitters include 4,4'-bis(*N*-carbazolyl)biphenyl (CBP) and *N,N,N',N'*-tetraphenylbenzidine (TAD) with T_1 triplet state energies of 2.6 and 2.4 eV, respectively. Known host materials for blue emitters are also frequently based on carbazole or triphenylamine moieties.²⁻⁵ In derivatives with disrupted or reduced conjugation, the triplet energies can be raised to about 2.9–3.0 eV, thus rendering them suitable for blue-emitting phosphorescent dyes.^{3,4} Such materials include CDBP (4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl), metaCBP (3,3'-bis(9-carbazolyl)biphenyl), mCP (3,5-bis(9-carbazolyl)benzene), and the polymer poly(vinylcarbazole),⁶⁻¹⁵ all based on carbazole as chromophore. Similar triphenylamine-based derivatives are also employed in OLEDs.¹⁶

Despite the ubiquitous use of these materials, the spectroscopic understanding of their excited states is limited.^{1,3,17,18} Carbazole and triphenylamine-based hosts have a tendency to form excimers^{12,14} that may impact on

the performance of OLEDs.¹⁹ While excimer-formation in carbazole and triphenylamine is well-known,^{20,21} it is less clear why some of their derivatives are more susceptible to the formation of excimers than others.

To obtain a more thorough understanding of the electronic properties of carbazole- and triphenylamine-based host materials, we have investigated two systematic series (Figure 1) where the degree of coupling between two triphenylamine or carbazole chromophores is modified gradually. To this end, we have complemented CBP and TAD with a spiro-substituted derivative where the central two phenyl rings of the CBP are forced into planarity, and with a CH_3 -substituted derivative that increases the twist between the two central phenyl rings and so disrupts conjugation. Thus, the carbazole-based series consists of the *N*-phenylcarbazole (NPC) as reference compound, CDBP, CBP, and Spiro-2CBP, with electronic coupling between two NPC units increasing along the series. The analogous triphenylamine-based series is provided by comparing triphenylamine (TPA) with TDAD, TAD, and Spiro-TAD. Based on phosphorescence measurements supplemented by density-functional theory (DFT) calculations we find that an increase in planarity of the central biphenyl is associated with localization of the excitation there that efficiently prevents the formation of excimers. This is in contrast to the derivatives with CH_3 substitution on the 2- and 2'-position of the biphenyl unit,

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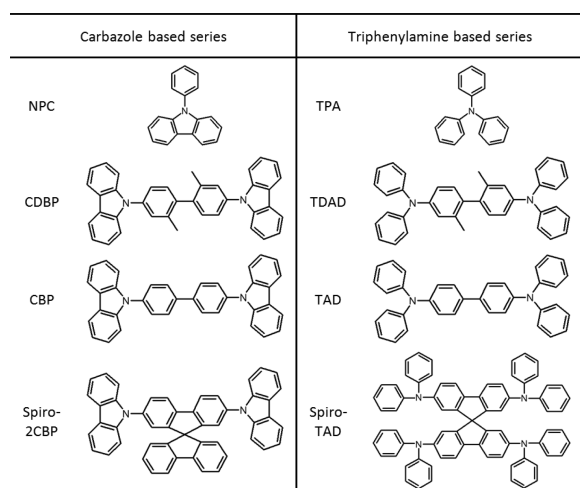


Figure 1. Chemical structures and abbreviations of the molecules used.

where the excitation localizes on the carbazole or triphenylamine moiety so that excimers are formed readily. Thus, in contrast to the common view,⁵ for the host materials based on *N*-phenylcarbazole and triphenylamine, introducing steric twisting *increases* the propensity to excimer formation.

II. EXPERIMENTAL SECTION

Materials. Triphenylamine (TPA), 2,2',7,7'-tetrakis(*N,N*-diphenylamino)-9,9-spirobifluorene (Spiro-TAD), *N*-phenylcarbazole (NPC), 4,4'-bis(*N*-carbazolyl)-biphenyl (CBP), 2,7-bis(carbazol-9-yl)-9,9-spirobifluorene (Spiro-2CBP), polystyrene (PS), tetrahydrofuran (THF), hexane, and acetonitrile (ACN) were obtained from Sigma-Aldrich. TAD was supplied by Tokyo Chemical Industry CO., Ltd. 4,4'-Bis(9-carbazolyl)-2,2'-dimethylbiphenyl (CDBP) was synthesized as described by Schrögel et al.¹¹ *N,N,N',N'*-(Tetraphenyl)-2,2'-dimethylbenzidine (TDAD) was synthesized according to the procedure described below. The structures of all molecules are presented in Figure 1.

Synthesis of *N,N,N',N'*-(Tetraphenyl)-2,2'-dimethylbenzidine (TDAD). 4,4'-Diodo-2,2'-dimethylbiphenyl (3.00 g, 6.7 mmol),¹¹ diphenylamine (2.60 g, 15.2 mmol), potassium carbonate (7.50 g, 54.4 mmol), copper powder (1.75 g, 27.6 mmol), and 18-crown-6 (1.41 g, 5.3 mmol) were refluxed in 50 mL of *o*-dichlorobenzene in an argon atmosphere for 96 h. Copper and inorganic salts were filtered off and the solvent was evaporated. Excess diphenylamine was removed with hot ethanol. Column chromatography on silica gel with hexane/DCM (2.5:1) as eluent yielded 1.65 g (48%) of the product as white solid. Further purification was carried out by zone sublimation. EI-MS *m/z*: 516 (100, M⁺), 258 (40, M2⁺). EI-MS *m/z*: 516 (100, M⁺), 258 (40, M2⁺). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.30–7.22 (m, 8H), 7.16–7.10 (m, 8H), 7.05–6.97 (m, 8H), 6.94–6.89 (m, 2H), 2.00 (s, 6H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 148.27, 146.81, 137.43, 136.25, 130.75, 129.51, 125.43, 124.50, 122.84, 121.55, 20.42.

Sample Preparation and Spectroscopic Measurements. The concentration of the compounds in the hexane solutions was 10⁻⁵ M. Films comprising 2 wt % of the materials under investigation in polystyrene (PS) were prepared by spin-coating from tetrahydrofuran (THF) solution. Absorption and fluorescence spectra were recorded on a Varian Cary 5000 spectrophotometer and a Jasco FP-8600 spectrofluorimeter,

respectively. Phosphorescence at 77 K was measured with a Jasco spectrofluorimeter equipped with a liquid nitrogen cooling unit (PMU-830).

Computational Methods. Density functional theory (DFT) calculations with the Coulomb attenuated CAM-B3LYP exchange-correlation functional and a split valence 6-31G* basis set were performed to obtain the optimized ground state geometry for the CBP, CDBP, TAD, and TDAD molecules without any symmetry constraints imposed. Vibrational frequency calculations were used to characterize the stationary points and no imaginary frequencies were found. Excited state energies for the singlet and triplet vertical transitions and optimized geometries for the S₁ and T₁ state were calculated with linear response time-dependent density functional theory (TD-DFT). A natural transition orbital analysis was used to visualize the excited state localization. Additionally ground state DFT calculations with a triplet multiplicity were used to compare with the geometry obtained at the TD-DFT level. All calculations were performed with the Gaussian 09 program²² and the Avogadro molecular editor was used to visualize the orbitals.²³

III. RESULTS AND DISCUSSION

Spectroscopy of Carbazole-Based Hosts. To obtain a deeper understanding on the impact of twisting, we shall first consider the carbazole-based series. Figure 2 displays the absorption and fluorescence spectra obtained in hexane solution along with the phosphorescence spectra measured in a polystyrene matrix at 77 K. The spectrum of the reference compound *N*-phenylcarbazole is fully consistent with those reported earlier for *N*-ethylcarbazole.^{24,25} The small Stokes'

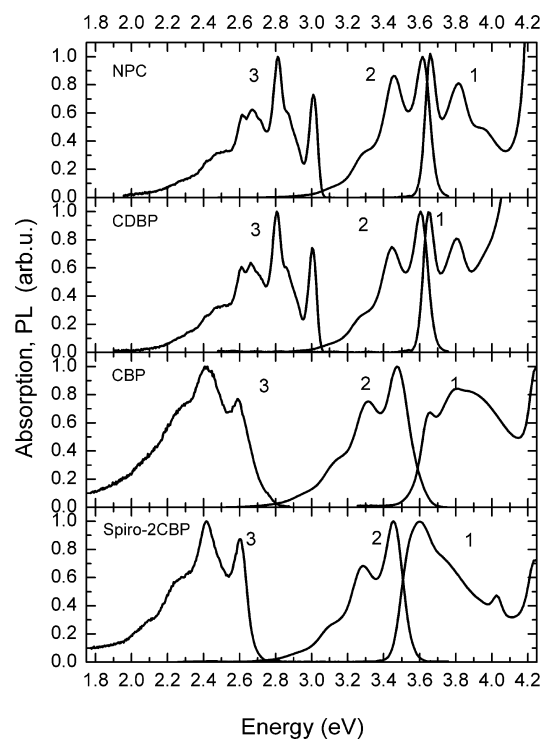


Figure 2. Absorption (1), fluorescence (2), and phosphorescence (3) of NPC, CDBP, CBP, and Spiro-2CBP. Absorption and fluorescence were measured in hexane at room temperature (concentration $c = 10^{-5}$ M). Phosphorescence spectra were obtained at 77 K in PS matrix ($c = 2$ wt %).

shift of 30 meV between absorption and emission and the well-resolved vibrational structure reflect the rigidity of the carbazole moiety. The spectra obtained for CDBP are identical with those of *N*-phenylcarbazole, except that absorption and fluorescence are shifted slightly to lower energies by 10 meV. In the CBP, the 0–0 and 0–1 peaks of the S_0 – S_1 absorption coincide with those in CDBP, yet the spectral weight of the 0–1 is increased and it merges into a shoulder at about 3.9 eV, previously associated with absorption involving the central biphenyl unit.¹¹ In contrast, the fluorescence of CBP is shifted strongly to lower energies compared to CDBP by 130 meV, and the Stokes' shift increases to 185 meV, all quantities measured from the 0–0 positions. The difference in the phosphorescence spectra is even more pronounced. While CDBP has the 0–0 peak of the T_1 state at 3.00 eV, it is about 410 meV lower, i.e. at 2.59 eV for CBP. In fact, the phosphorescence of CBP is in position and shape nearly identical with that of Spiro-2CBP, and also the fluorescence spectra differ by only 20 meV. The absorption of Spiro-2CBP resembles a broadened mirror image of the fluorescence. If one associates the peak at 3.55 eV with the 0–0 transition of the absorption of Spiro-2CBP, the Stokes' shift is reduced to about 150 meV in Spiro-2CBP, reflecting its more rigid nature compared to CBP, where the Stokes' shift is 180 meV.

What insight can be obtained from the comparison of these spectra? The torsion angles between the two central phenyl rings in CDPB, CBP, and Spiro-CBP in the ground state geometry are 82°, 33°, and about 0°, respectively.¹¹ Evidently, the close similarity of the CDBP spectra with the NPC spectra results from poor electronic coupling between the two almost orthogonal central phenyl rings, so that each half of the molecule forms an electronically nearly isolated chromophore. In a similar way, the spectral and energetic proximity of the fluorescence and phosphorescence of the Spiro-2CBP with CBP suggests a nearly planar conformation of CBP after excitation. The coincidence of the 0–0 absorption peak in CBP with that in CDPB, yet of the 0–0 fluorescence peak in CBP with that in Spiro-2CBP and the concomitant large Stokes' shift further support this assignment. Thus, in CBP, absorption dominated by the *N*-phenylcarbazole unit and the twisted biphenyl is followed by geometric relaxation into a planar geometry akin to Spiro-2CBP, from which emission takes place. With this insight, the larger bathochromic shift of the phosphorescence compared to the fluorescence when going from CDBP to CBP can be understood. The moderate S_1 – T_1 gap in *N*-phenylcarbazole of 0.6 eV is usually attributed to admixtures of n – π^* transitions and associated reduced electron–hole wave function overlap in the excited states.²⁶ The much larger S_1 – T_1 gap of 0.9 eV in CBP and Spiro-2CBP indicates a stronger contribution of π – π^* transitions with concomitantly larger electron–hole wave function overlap in the planar geometry.

Spectroscopy of Triphenylamine-Based Hosts and Comparison to Carbazole-Based Hosts. It is interesting to consider whether the same electronic changes occur in triphenylamine-based host materials when the coupling between two adjacent units is reduced. Superficially, triphenylamine (TPA) differs from *N*-phenylcarbazole merely by the carbon–carbon-linkage that forces two phenyl rings into planarity, yet this leads to pronounced differences in the optical spectra as shown in Figure 3. The absorption of TPA has a weak feature in the absorption tail at about 3.7 eV followed by a strong broad peak at 4.13 eV. The unstructured

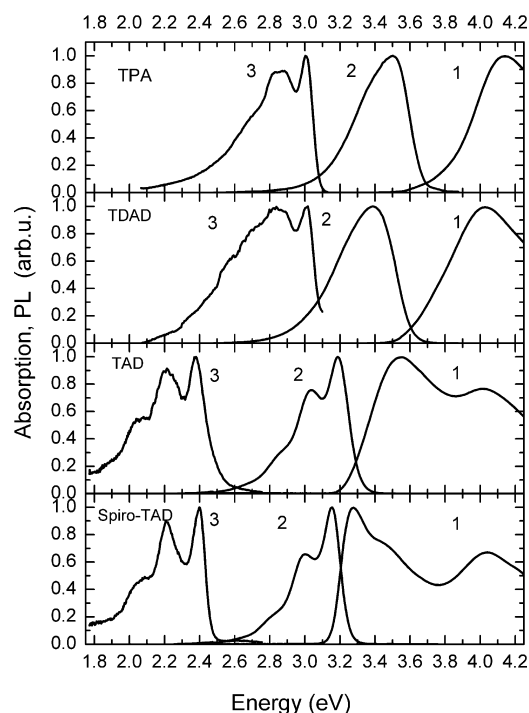


Figure 3. Absorption (1), fluorescence (2), and phosphorescence (3) of TPA, TDAD, TAD, and Spiro-TAD. Absorption and fluorescence were measured in hexane at room temperature ($c = 10^{-5}$ M). Phosphorescence spectra were obtained at 77 K in PS matrix ($c = 2$ wt %).

broad emission peaks at 3.5 eV. The phosphorescence, measured at 77 K in a polystyrene matrix, shows more vibrational structure and peaks at 3.0 eV. When moving from TPA to TDAD, we observe the same trend as seen for the transition from NPC to CDBP. That is, the phosphorescence spectrum remains identical in position, merely the absorption and fluorescence shift to lower energies by a small amount (10–20 meV), and the spectra largely retain their shape. Analogous to the changes occurring when going from CDBP to the more planar CBP, we observe clear spectral changes and shifts when going from TDAD to TAD. The fluorescence and phosphorescence shift by 200 and 631 meV to the red, respectively, and the vibrational structure is modified. The absorption also shows a strong redshift (477 meV). Also analogous to the transition from CBP to Spiro-2CBP, the fluorescence and phosphorescence spectra of TAD and Spiro-TAD are nearly identical in position and shape, and the absorption of Spiro-TAD is a broadened mirror image of the emission.

Evidently, the data for the triphenylamine derivatives can be interpreted analogously to those of the carbazole-based derivatives, i.e., joining two TPA units in a strongly twisted way as is the case for TDAD leads, unsurprisingly, to marginal electronic coupling between both halves of the molecule. Omitting the CH_3 groups in the central biphenyl as in TAD allows for geometric relaxation so that fluorescence and phosphorescence occur from the molecule with a planar geometry in the center as for Spiro-TAD. This is accompanied by a strong increase in S_1 – T_1 splitting to about 0.8 eV that indicates a dominant contribution of π – π^* transitions in TAD and Spiro-TAD,^{27,28} in contrast to the lower S_1 – T_1 splitting of 0.5 and 0.4 eV, respectively, in TPA and TDAD, that is

characteristic for strong admixtures of $n-\pi^*$ transitions.²⁶ This result is consistent with reports that the spectroscopic features measured for Spiro-TAD correspond to electronic transitions centered on the diaminofluorene moiety.^{29,30}

To facilitate the interpretation of these data, the spectra for the two limiting cases, the single chromophore, and the fully planarised linked bichromophore are compared in Figure 4.

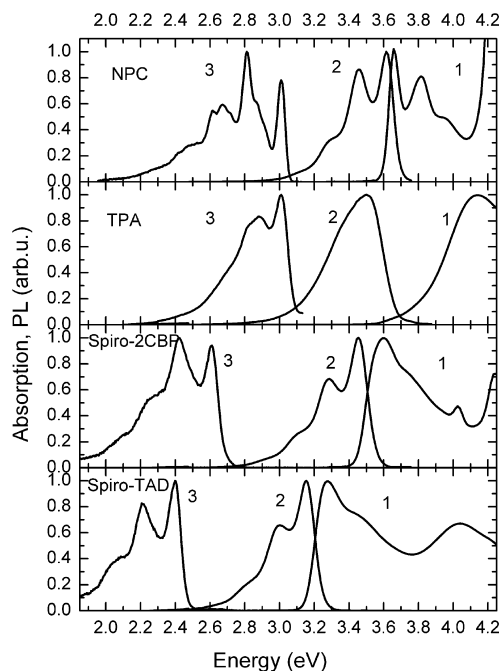


Figure 4. Absorption (1), fluorescence (2), and phosphorescence (3) of NPC, TPA, Spiro-2CBP, and Spiro-TAD. Absorption and fluorescence were measured in hexane at room temperature ($c = 10^{-5}$ M). Phosphorescence spectra were obtained at 77 K in PS matrix ($c = 2$ wt %).

The similarity between the spectra for the carbazole and triphenylamine based spiro-derivatives is striking. The fact that the choice of the outer group (triphenylamine or carbazole) has little effect on the spectral shapes confirms the notion that for the spiro-derivatives, the optical transitions originate largely from the diaminofluorene center. A noteworthy feature is the overall lower energy for the Spiro-TAD compared to Spiro-2CBP. Evidently, the flexibility of the two outer phenyl rings allows for some degree of conjugation through the amines that is not possible for the more rigid carbazole. We consider that this torsional degree of freedom is also the reason why the fluorescence of TPA is broadened and red-shifted compared to the well-structured NPC-fluorescence. The increased broadening is also manifested in the phosphorescence of TPA, though there is no further energy shift, which we attribute to the generally rather localized nature of the triplet excited state.³¹ We also assign the large Stokes' shift in TPA and the rather small Stokes' shift in NPC to the differences in the torsional degrees of freedom of the phenyl rings, as discussed by Gierschner et al.³²

Effect of Torsion on Excimer Formation. By comparison to the reference compounds NPC/Spiro-2CBP and TPA/Spiro-TPA, we were able to assess the spectral effects of increasing torsion between the two central phenyl rings on the phosphorescence, fluorescence, and absorption for the carbazole and triphenylamine derivatives CBP/CDBP and

TAD/TDAD in polystyrene *matrix* or hexane *solution*. This enables us to now consider the effect torsion has on the formation of excimers in the *neat films* of these typical OLED host materials. Figure 5 compares the 77 K phosphorescence

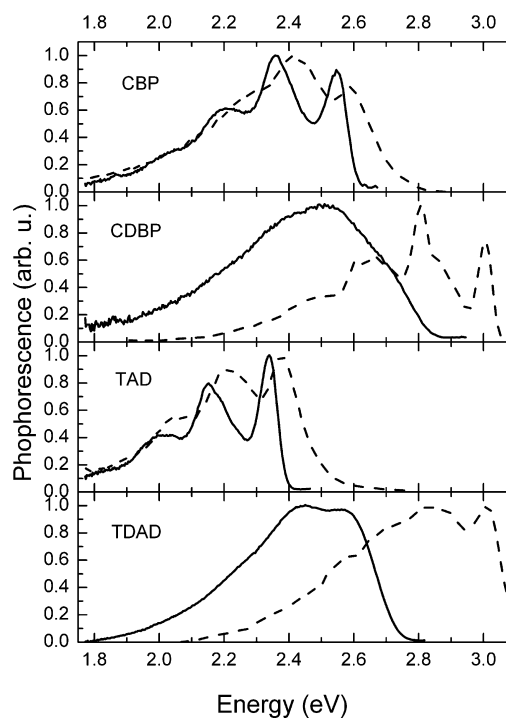


Figure 5. Phosphorescence spectra of films of CBP, CDBP, TAD, and TDAD measured at 77 K. Dashed lines represent the phosphorescence spectra of 2% solid solution in PS and solid lines refer to neat films.

spectra of CBP and CDBP obtained in neat films with those obtained in a polystyrene matrix. The same is also displayed for TAD and TDAD. For the two derivatives CBP and TAD, the neat film spectra exhibit a shift to lower energies by about 40 meV when going from polystyrene matrix to neat film. This polarization effect is similar to solvatochromism and is well understood. In contrast to CBP and TAD, the well-structured phosphorescence spectra of the strongly twisted derivatives CDBP and TDAD, with the 0–0 peak near 3.0 eV in polystyrene, lose most of their vibrational structure and shift significantly to the red.

For CDBP, the broad emission centered around 2.5 eV had previously been shown to arise from a superposition of a small contribution of monomer emission (0–0 at 3.0 eV) and a dominant contribution of excimer emission (centered at 2.5 eV).¹² Comparison with model carbazolophanes has shown that the excimer can be attributed to a sandwich-type arrangement between two carbazole moieties.²⁴ The propensity of carbazole to form excimers or dimers is well documented.^{33,34} The stronger tendency of CDBP to excimer formation compared to CBP is remarkable, given that CDBP is less prone to crystallization than CBP.¹¹

The similarity in spectral changes when going from TAD to the more twisted TDAD leads us to infer that the emission in neat films of TDAD may be attributed to a triphenylamine-based excimer. In fact, Burkhard and Jhon identified broad excimer emission from triphenylamine centered at 2.7 eV, suggesting that it arises by interaction of nitrogen atom with the aromatic rings of the neighboring molecule in close proximity.²¹

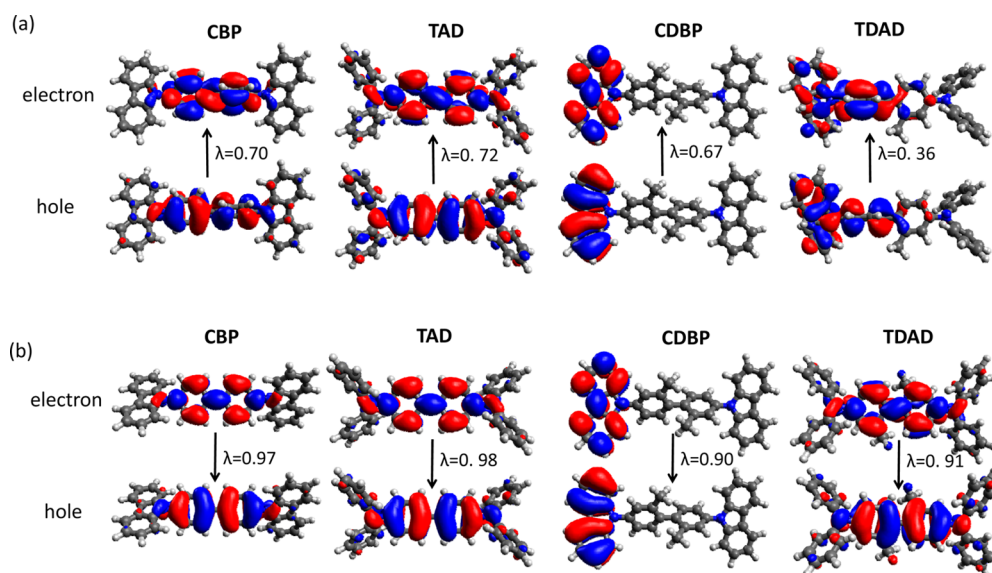


Figure 6. Dominant electron–hole pair natural transition orbitals (NTOs) of CBP, TAD, CDBP, and TDAD, for the triplet T_1 excited state, calculated by TD-DFT (CAM-B3LYP/6-31G*) (a) for the S_0 ground state geometry and (b) for the relaxed T_1 excited state geometry. The λ eigenvalues quantify the relevant contribution of the pair to the excitation. Additional NTO pairs are provided in the Supporting Information.

Thus, on the basis of the spectroscopic data we have obtained the following information. In the strongly twisted derivatives CDBP and TDAD, the fluorescence and phosphorescence is dominated by the individual properties of the outer *N*-phenylcarbazole and triphenylamine moieties. There is little coupling between two halves of the molecule. These twisted derivatives show excimer formation in neat films. In contrast, the fluorescence and phosphorescence of CBP and TAD is dominated by the properties of the planarized central part of the molecule, and these compounds do not show excimer formation in thin films.

DFT and TD-DFT Calculations. To gain a more comprehensive understanding, we calculated the excited states of CBP, CDBP, TAD, and TDAD in the gas phase using TD-DFT. The natural transition orbitals (NTO) method provides an elegant way of visualizing the localization of the excited state.³⁵ It builds on representing the excited state by a set of orbitals obtained by a singular value decomposition of the transition density matrix and allows for a simple electron–hole pair representation of the excitation. Figure 6 shows the NTOs for the vertical transition $S_0 \rightarrow T_1$, calculated using the ground state optimized geometry, and the $T_1 \rightarrow S_0$ transition, calculated at the T_1 TD-DFT optimized geometry. The dihedral angles at the ground state between the phenyl rings are 39° for CPB, 38° for TAD, 90° for CDPB, and 89° for TDAD. The comparison of the computational results obtained for the two geometries with the experimental results turns out to be informative. For CBP and TAD, the gas phase calculations predict a planarization after excitation. The dihedral angles of the central biphenyls reduce to 2° and 1.5° for CBP and TAD, respectively. A planarized excited state geometry is consistent with the experimentally observed similarity to the emission of the spiro-derivatives. Importantly, for both geometries the calculations suggest the triplet excited state is associated with a hole that is delocalized and an electron that is localized mainly onto the central biphenyl. This is fully consistent with the experimental finding that the fluorescence and phosphorescence of CBP and TAD are dominated by the properties of the planarized central part of the molecule. This is

also consistent with the strong dependence of the fluorescence of CBP and TAD on solvent polarity, in contrast to CDBP and TDAD (see the Supporting Information).

We now turn our attention to the strongly twisted compounds CDBP and TDAD that have the biphenyl rings in an orthogonal configuration in the S_0 ground state. For CDBP, interestingly, the excited state optimization, starting from the S_0 ground state geometry, leaves the biphenyl dihedral angle unaffected and the NTOs are similar to those of the ground state geometry, i.e. localized on the carbazole part. For TDAD, however, in the relaxed excited state geometry the molecular axis bends significantly to decrease the steric interaction between methyl groups and hydrogens and allow for a dihedral angle of 150° (measured relative to the *cis* conformation of the methyl groups). We will call this relaxed structure geometry A. The NTOs obtained for geometry A differ strongly from the NTOs obtained using the ground state geometry. Whereas for the ground state geometry the triplet excited state seems to involve transitions between only one of the triphenylamine unit, with minor involvement of the central phenyl unit of the other TPA, the calculations for the relaxed excited state geometry suggest transitions from the central biphenyl moiety to be dominant. Geometry A, however, does not agree with the spectroscopic observations. The spectroscopic data clearly indicate that the phosphorescence is dominated by the individual properties of the outer triphenylamine moieties. This is evident from the vibrational structure and energy in matrix films as well as from the propensity to excimer formation in neat films. Clearly, the conformation prevailing after excitation in the condensed phase is closer to the orthogonal singlet ground state geometry than to the fully relaxed, more planarized conformation derived by optimizing the T_1 excited state geometry at the TD-DFT level in the gas phase. Thus, it appears that in the condensed phase conformational changes of a molecule are more restricted than in the gas phase, in particular with respect to bending of the molecular axis. To explore the potential energy landscape of the TDAD T_1 excited state further, we optimized the geometry at the DFT level. This reveals that there is another energetically

favorable local minimum that allows for a torsion angle of 65° between the rings, which we call geometry B. On the basis of this structure, the NTOs shown in Figure 7 suggest a localization that resembles the NTOs obtained for the singlet ground state geometry.

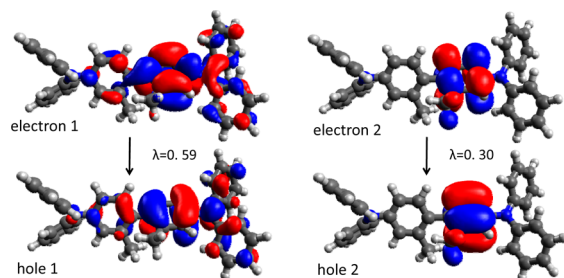


Figure 7. Natural transition orbitals (NTOs) of TDAD calculated using the T_1 geometry optimized at the DFT (CAM-B3LYP/6-31G*) level with 65° torsion between the central biphenyl rings. λ gives the relevant contribution of the pair to the excitation.

To summarize the information we get by modeling the excited state structures, the following general observations can be made regarding the changes in geometry upon relaxation of the excited state for the four molecules studied here: (i) It is the central biphenyl part that accommodates most geometrical changes and controls the exciton localization. Indeed, the C–C bond length between the central phenyl rings decreases in the excited state when the torsion between the rings decreases, and the bond lengths between the central phenyl rings and the N atom in the triphenylamine or carbazole unit decrease. The bond lengths in the carbazole units and the two outer rings of the triphenylamine units remain almost identical with the ground state values. (ii) For TAD and TDAD both in the ground and excited state geometry the amine keeps a planar conformation, i.e. the three C–N–C bond torsions around each N remain at $\sim 120^\circ$ each (the N retains an sp^2 hybridization), therefore keeping the propeller structure of the TPA unit.³⁶ Further information on the geometries can be found in the Supporting Information where we collect all the relevant bond lengths and torsion angles in the ground state and excited state. We finally remark that a similar behavior regarding the role of the central phenyl rings has been reported in an early computational study of hole polaron relaxation in the TDP (*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine) molecule³⁷ while for the same molecule the singlet excited state has been characterized at the CIS³⁸ and TD-DFT³⁹ level. The triplet excited state of biphenyl has also been investigated with DFT⁴⁰ predicting a planarized excited state structure.

We now turn to comparing the triphenylamine-based compounds TAD and TDAD with their carbazole-based analogues CBP and CDBP. The experimental data have suggested there to be some higher degree of conjugation in the triphenylamine-based derivatives. This is further supported in the DFT calculations. For TAD, we observe the electron-NTO to extend through the nitrogen atom into the phenyl moieties, in contrast to CBP. Similarly, for TDAD some conjugation prevails through the nitrogen in contrast to CDBP. This applies to both ground and excited state geometries. For all molecules, the C–N bond lengths with the central phenyls are the same and the N has an sp^2 hybridization, yet in TAD and TDAD the two outer phenyl rings of the TPA unit can

adopt a torsion angle of only $38\text{--}40^\circ$ with respect to the central phenyl, whereas the rigid carbazole unit is placed at $50\text{--}55^\circ$ to the central phenyl.

IV. CONCLUSION

The spectroscopic investigations of CBP/CDBP and TAD/TDAD have the aim to clarify the stronger propensity to excimer formation that has been observed in CDBP and TDAD compared to CBP and TAD. In CDBP and TDAD the two phenyl rings of the central biphenyl are strongly twisted. Inducing steric twist in the biphenyl is a convenient means to obtain a high T_1 energy. The observation that such steric twisting induces excimer formation rather than preventing it is, at first, counterintuitive.

By comparing these materials to the fully planar/fully disjointed reference compounds Spiro-2CBP/NPC and Spiro-TAD/TPA, we could ascertain that with increasing degree of torsion between the central biphenyls the excitation moves from being localized in the central part of the molecule toward the outer *N*-phenylcarbazole/triphenylamine part. This insight was gained on the basis of spectroscopic measurements and is further substantiated by quantum chemical calculations. While the localization of the excitation onto the outer *N*-phenylcarbazole/triphenylamine part in the more twisted compounds serves to increase the T_1 energies to the high values of 3.0/3.1 eV known for NPC/TPA, we suggest that the increased electron density on the outer *N*-phenylcarbazole/triphenylamine part is also the cause for the observed tendency of CDBP and TDAD to form excimers in neat films, while no such excimer formation seems to occur for CBP and TAD that lack electron density on the periphery of the molecule. Further work will be needed to clarify to what extent the propensity to excimer formation resulting from the steric twist in CDBP and TDAD also impacts on their performance as charge-transferring and matrix materials.

■ ASSOCIATED CONTENT

Supporting Information

Figures showing the dominant electron–hole pair natural transition orbitals (NTOs), as well as bond lengths and dihedral angles, of CBP, TAD, CDBP, and TDAD, calculated with TD-DFT (CAM-B3LYP/6-31G*), once on the basis of ground state optimized geometries for the $S_0 \rightarrow T_1$ transition, and once on the basis of optimized triplet T_1 geometries for the $T_1 \rightarrow S_0$ transition; further, bond lengths and dihedral angles of CBP, TAD, CDBP, and TDAD for the DFT (CAM-B3LYP/6-31G*) optimized T_1 geometry are shown; the corresponding data are also given for the singlet transitions, i.e. figures showing the dominant electron-hole pair NTOs of CBP, TAD, CDBP, and TDAD for the $S_0 \rightarrow S_1$ transition, calculated with TD-DFT (CAM-B3LYP/6-31G*) on the basis of ground state optimized geometries and on the basis of S_1 optimized geometries; to address the charge-transfer character, the absorption and fluorescence spectra of CBP, CDBP, TAD, and TDAD in the nonpolar solvent hexane, the more polar solvent THF, and the strongly polar solvent acetonitrile are displayed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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