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Planarized and Twisted Intramolecular Charge Transfer – A Concept for Fluorophores Showing Two Independent Rotations in Excited State

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ABSTRACT: TICT (twisted intramolecular charge transfer) compounds are characterized by showing a rotation around a single bond in excited state: starting from an almost planar geometry in ground state, a twisted system is formed in the electronically excited state. The previous reported PLICT (planarized intramolecular charge transfer) compounds show inverse behavior: starting from a twisted geometry in the electronically ground state, a planarized system is formed in the excited state by rotation around a single bond. Here, we present a concept of the planarized and twisted intramolecular charge transfer (PLATICT) states which amalgamates both (TICT and PLICT) effects. Due to an intramolecular charge transfer, both a twisting around one single bond and a planarization around another one occurs. In sum, the PLATICT system shows two independent rotations around different axes in the excited state. By means of quantum chemical calculations (TD-cam-B3LYP and CC2) and experimental studies, we could demonstrate that N-aryl-substituted 1-aminoindoles are able to form photoinduced PLATICT states. In the fluorescence spectra of N-aryl-substituted 1-aminoindoles with a methoxycarbonyl or a cyano group as substituent in the aryl ring, very large Stokes shifts (ca. 18000 cm⁻¹; >250 nm) are observed. The two independent rotations in excited state, the very large Stokes shifts and their easy availability starting from indoline, make them very attractive for the use as optical switches and motors in various fields of chemistry.

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Introduction

Fluorophores are used to detect, identify and characterize structures and functions of inorganic and organic molecules as well as biological systems.^{[1],[2]} In general they show a small Stokes shift, which is defined as the gap between the maximum of the first absorption band and the maximum of fluorescence.^[1] Larges Stokes shifts are observed when an intramolecular relaxation process in an electronic excited state leads to an energy minimum, which is far away from the initial geometric parameters. Such a relaxation could be a rotation around a single bond in the excited state. A very prominent example for an organic molecule showing this type of rotation is 4-(dimethylamino)benzonitrile (DMABN, 1).^{[3],[4],[5]} In non-polar solvents, the fluorescence spectrum of DMABN exhibits only a single band from locally excited (LE) state. The electronic excited molecule in the LE state shows differences only in bond length and bond angles, but not in the relative orientation of parts of the molecule. Therefore, the LE emission band exhibits only a small Stokes shift. In more polar solvents, beside the "normal" band, an additional red-shifted band is observed. This "anomalous" emission band can be interpreted by following model: The excitation by irradiation leads to an intramolecular charge transfer from the donor group D to the acceptor moiety A (see Figure 1a).^{[4],[5]} The resulting diradical I* stabilizes itself by rotation of ca. 90° around the single bond resulting in the twisted intramolecular charge transfer (TICT) state II*. The driving force for this rotation around the single bond is the minimization of the Coulomb interaction between the two unpaired electrons.^[4] The geometric relaxation results in large Stokes shifts of the TICT fluorescence.^{[6],[7],[8],[9]} As the rotation leads to orbitally decoupled π systems of the donor and acceptor units, the emission from TICT state to ground state is overlap forbidden.^{[4],[5]} A small TICT fluorescence quantum yield is therefore expected. The observed TICT fluorescence occurs mainly from molecules in excited vibrational states.^{[4],[5]}



Figure 1. Schematic representation of the change in the geometrical arrangement of the donor groups D and D' as well as the acceptor group A upon going from the ground state to a TICT (a) and PLICT state (b). As examples 4-(dimethylamino)benzonitrile (DMABN, 1) and 1-aminoindole (2) are shown.

Recently, we introduced a second concept for a rotation of ca. 90° around a single bond in an electronic excited state. As model compounds 1-aminoindole (2) and its derivatives (see Figure 1b) were used.^[10] Here, two donor groups (D and D') are connected by a single bond. In the electronic ground state (I), the repulsive interaction between the electron pairs of the donor groups D' and D results in a twisting of these groups. The electronic excitation leads to the intramolecular charge transfer from the donor group D' to the acceptor moiety A. The thus formed state I* does not represent a minimum on the potential energy surface and immediately passes into the planarized intramolecular charge transfer (PLICT) state (II*) via rotation around the N-N single bond.^[10] This adiabatic relaxation process leads to a strong Stokes shift which can also be recorded in non-polar solvents. Furthermore, in contrast to the TICT compounds, the emission from the PLICT state to the ground state is allowed and hence the guantum yields for the observed fluorescence are high.^[10]

Both the TICT and the PLICT systems can be considered as ultrafast fluorescence rotors.^{[11],[12],[13]} However, as they exhibit only a 90° forward and back rotation, they are not suitable for the design of an ultrafast molecular motor. Here, either a unidirectional 360° rotation process around one axis or a combination of two independent rotations around different axes is required.^[14] The first case describes a molecular rotation motor,^[15] the latter case a molecular pushing motor.^[16] In search of suitable rotations for the design of fast molecular pushing motors^[17] we got interested in systems showing two independent rotations around different axes in the excited state. Here we describe a concept in which we merge the principle of the TICT states and the PLICT states. The resulting system undergoes in the excited state both a twisting around one single bond and a planarization around another single bond. These two rotation processes should also result in very large Stokes shifts of the fluorophores. We assumed that systems meeting the above combination (TICT & PLICT) are substituted N-aryl-1H-indol-1-amines. In the present work the fluorescence of some Naryl-substituted 1-aminoindoles were investigated by means of quantum chemical calculations (TD-B3LYP, TD-cam-B3LYP and CC2). Furthermore we synthesized some Naryl-substituted 1-aminoindoles, recorded their fluorescence spectra in different solvents and compared the experimentally data with the calculated ones.

Results and Discussion

a) Concept

Our idea for the combination of both states (TICT and PLICT) is depicted in Figure 2a. From the chemical point of view, such a system should have one donor group D coupled to the acceptor group A and to the donor group D'. The latter is fused to the acceptor unit A'. In the ground state (I), the donor group D and the acceptor group A are in the same plane (θ_2 (N1-

N8-C9-C10) = 0°), whereas the donor group D' is perpendicular to D (θ_1 (C2-N1-N8-C9) = 90°). The concurrent presence of both structural elements (D-A for TICT state and D-D'-A' for PLICT state) should lead to an amalgamation of the TICT and the PLICT process in the electronic excited state. Let's assume that the excitation of one electron from donor D to the acceptor A leads to the state I* in which the donor D exhibits a positive charge. The stabilization of this state can occur in different ways. In the first case (path *a*), the TICT state II* is formed by rotation around the single bond between the donor D⁺ and the acceptor A⁻ which corresponds to a twisting of the D⁺-A⁻ subunit (θ_2 (N1-N8-C9-C10) = 90°).



Figure 2. Principle of the **pl**anarized **a**nd twisted intramolecular **c**harge transfer (PLATICT) states. a) Schematic representation of the change in the geometrical arrangement of the donor groups D and D' as well as the acceptor group A upon going from the ground state (I) to **pl**anarized **a**nd twisted intramolecular **c**harge transfer (PLATICT) states (**IV***). The direct path *b* from **I*** to **IV*** corresponds to a concerted pathway. b) Substituted *N*-aryl-1*H*-indol-1-amines are possible examples for PLATICT compounds.

In the second case (path *c*), the PLICT state III* is formed due to interaction between the positively charged D^+ and the donor group D'. The rotation around the D^+ -D subunit results in

a planarization of this unit (θ_1 (C2-N1-N8-C9) = 0°). State II* as well as state III* can be further stabilized: the TICT state (II*) by planarization of the subunit D⁺-D and the PLICT state (III*) by twisting of the subunit D⁺-A⁻. In both cases the result is the formation of the **pl**anarized **a**nd twisted intramolecular charge transfer (PLATICT) state IV* (θ_1 (C2-N1-N8-C9) = 0° and θ_2 (N1-N8-C9-C10) = 90°). Furthermore, a direct path (*b*) from I* to IV* corresponding to a concerted pathway is also possible (Figure 2).

The deexcitation of the PLATICT state (IV^*) can occur either by radiative or non-radiative transition. Due to the twofold rotations in the excited state, the resulting fluorescence should feature a very large Stokes shift. The then formed state IV is labile and converts through two independent rotations (via path *d*, *e* or *f* in Figure 2) into the starting state **I**.

b) Theoretical Investigation of the PLATICT States

We assumed that N-aryl-substituted 1-aminoindoles represent systems, which should be able to form a planarized and twisted intramolecular charge transfer (PLATICT) state (Figure 2b). Here, two planar systems are linked via their donor units. In the ground state, the indole unit (donor group D' and acceptor group A') should be perpendicular to the aniline system (donor group D and acceptor group A). The whole system possesses both a TICT unit, which is represented by the aniline, and a PLICT system, which is represented by the 1-aminoindol. The nitrogen atom N8 belongs to both systems (TICT and PLICT) and is therefore the key element for the whole PLATICT system. In order to verify the concept, the N-aryl-substituted 1-aminoindoles **3-6** (Figure 3) unsubstituted or having strongly electron withdrawing groups in the para position to the nitrogen atom N8 were investigated by means of quantum chemical methods. The geometry optimization of the electronic ground states S_0 of **3-6** were performed using Becke's three-parameter hybrid functional (B3LYP^[18]). The geometrical parameters of the excited states S_1 were calculated by means of the time-dependent density functional theory (TD-DFT^[19]). It is known that TD-B3LYP tends to underestimate chargetransfer excitation energies^[20] due to spurious self-interaction.^[21] However, the use of TD-B3LYP yields good agreement for the vertical excitation energies of the first excited singlet states of TICT and PLICT compounds such as 4-(dimethylamino)benzonitrile^{[22],[23]}, dialkylaminopyridines^[24] and 1-aminoindoles^[10]. Furthermore, the electronic ground states S_0 and the excited states S_1 were geometrically optimized by means of cam-B3LYP^[25]. This hybrid exchange-correlation functional using the Coulomb-attenuating method performs well for charge transfer excitations in systems, which B3LYP underestimates enormously.^[25] As basis set, the def2-TZVP^[26] was used for both functionals. Subsequent frequency calculations were carried out in the ground states and the electronic excited states to verify the nature of the stationary points. All optimized states have no imaginary frequencies. Furthermore, the electronic excitation energies of the B3LYP- and cam-B3LYP-optimized structures were computed at the approximate second-order coupled cluster (CC2^{[27],[28]}) levels. Here again the def2-TZVP basis set was used.

A comparison of the optimized ground state structures reveals that the structural parameters of all 1-aminoindoles **3-6** are very similar independent on the used functional (B3LYP or cam-B3LYP). Selected structural parameters and the molecular structures of the ground state of **3** and **6** obtained by using cam-B3LYP/def2-TZVP are depicted in Figures 3 and 4. In both molecules the most important requirement for the ground state of compounds, which are able to be transformed into PLATICT states, is fulfilled: The nitrogen atom N8 shows sp² hybridisation, its lone pair interacts with the phenyl ring and it is perpendicular orientated to the π system of the indole unit. Accordingly, the dihedral angle θ_2 (N1-N8-C9-C10) amounts to values close to 0° (-20° for **3** and -16° for **6**), whereas the dihedral angle θ_1 (C2-N1-N8-C9) is close to 90° (109° for **3** and 106° for **6**).



Figure 3. a) Structures of the 1-aminoindoles **3-6**. b) Structural parameters of the lowest singlet electronic states (ground, PLICT and PLATICT states) of the 1-aminoindoles **3** and **6** calculated using (TD)-cam-B3LYP.

Using the MO approximation, the transition from the ground state of **3** to the first exited single state (vertical excitation) is dominated by the (HOMO - 1) \rightarrow LUMO excitation according to CC2 results. Both orbitals are π and π^* orbitals and located at the indole system. In the case of the 1-aminoindole **6** the first exited single state (vertical excitation) corresponds to an excitation from (HOMO - 2) \rightarrow (LUMO + 1), whereby both orbitals are localized at the aminobenzonitrile unit.

In order to optimize the geometric parameters of the excited state S_1 by means of cam-B3LYP/def2-TZVP, the five energetically lowest excited singlet states were solved in each step and the lowest of them were used for optimization. As starting geometries structures showing different dihedral angles θ_1 and θ_2 were used. In the case of the aminoindoles **3** and **4** two [III* (PLICT) and IV* (PLATICT)] of the possible four (I*-IV*) states were identified as being minima on the energetic potential surface. For the aminoindoles **5** and **6** only the PLATICT state (IV*) shows an energetic minimum. Please note, that there are in each case two diastereomers of the PLICT and PLATICT states. Here, only the *anti* isomers in which the acceptor group A is orientated away from the phenyl ring of the indole unit are considered. The *syn* isomers show almost the same transition energies, Stokes shifts and oscillator strengths and are slightly energetically disfavored (Figure S1 and Table S1). In all cases, the TICT states of the aminoindoles **3-6** were no minima on the energetic potential surface.



Figure 4. a) Molecular structure of the ground (left), PLICT (middle) and PLATICT (right) states of the 1-aminoindole **3** calculated using (TD)-cam-B3LYP. b) Molecular structure of the ground (left) and PLATICT (right) states of the 1-aminoindole **6** calculated using (TD)-cam-B3LYP.

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The PLICT state of **3** and **4** can be considered as an intramolecular charge transfer from the pyrrole ring to the benzene ring of the indole unit^[29], whereby the thus generated positive charge in the pyrrole ring is stabilized by the lone pair of the nitrogen atom N8, which is part of the aniline system (see Figures 3 and 4). The display of the electron density difference between excited state and ground state at the PLICT geometry corroborated this assumption (Figure S3). This $\pi \to \pi^*$ transition results in an increase of the bond lengths C4-C5, C6-C7, N1-C7a and N1-C2 as well as a decrease of the bond lengths C5-C6 and C3-C3a in the indole ring. The bond lengths in the phenyl ring do not change significantly (Figure 3). The stabilization of the positive charge in the pyrrole ring by the lone pair of the nitrogen atom N8 causes a reduction of the N1-N8 distance. In the ground state the N1-N8 bond length amounts to 1.374 Å, whereas in the PLICT state the N-N bond has a value of only 1.325 Å. The PLICT state of **3** exhibits a dihedral angle θ_1 of 42°, which means that starting from the ground state a rotation of 67° has occurred (Figure 4). This intramolecular charge transfer can also be confirmed by the increase of the dipole moment. There is a significant change between the permanent dipole moments of the ground state of 3 (1.32 D) and the optimized PLICT state of 3 (6.71 D) (Table 1). The fact, that no PLICT states of 5 and 6 were found, can be easily explained as following: In the PLICT states the lone pair of the nitrogen atom N8 acts as electron donating unit. However, the methoxycarbonyl and cyano groups of 5 and 6 in para position also withdraw electrons from the nitrogen atom N8 causing a drastic reduction of its electron donating character.

The PLATICT states of the 1-aminoindoles can be considered as electron transfer from the lone pair of the nitrogen atom N8 to the phenyl group. The resulted singlet diradical is stabilized by two processes. The first one is a rotation around the dihedral angle θ_2 (N1-N8-C9-C10) in order to minimize the Coulomb interaction between the two unpaired electrons. The second process is a rotation around the dihedral angle θ_1 (C2-N1-N8-C9) to stabilize the positive charge at the nitrogen atom N8 by conjugation with the electron-rich π system of the indole unit. The dihedral angles θ_1 and θ_2 of the PLATICT compounds amounts to 0° and 100°, respectively, (see Figures 3 and 4). Starting from the ground states S_0 , this corresponds to two independent rotations by more than 100° in each case around two different axes.

The intramolecular charge transfer process is manifested by changes in the bond length. The occupation of a π^* orbital of the phenyl ring causes an increase in the distances C9-C10 and C11-C12 as well as a decrease in the distance C10-C11. With the exception of N1-C7a, the changes in the bond lengths of the indole ring are small. The stabilization of the positive charge of the nitrogen atom N8 by the electron-rich π system of the indole unit leads to an reduction of the N1-N8 bond distance by ca. 0.05 Å.

Table 1. Comparison between CC2 calculated and experimentally determined spectral properties of the aminoindoles **3-6**. The vertical singlet excitation ($S_0 \rightarrow S_1$) and emission ($S_0 \leftarrow S_1$) energies ΔE [cm⁻¹], Stokes shifts [cm⁻¹], oscillator strengths (*f*) and permanent dipole moments μ [D] of each state were computed by means of CC2/def2-TZVP//(TD)-cam-B3LYP/def2-TZVP. The absorption and fluorescence maxima as well as the quantum yields (Φ) were determined in different solvents.

	CC2 calculation					Experimental				
	State	μ[D]	Transition energy [cm ⁻¹]	Stokes shift [cm ⁻¹]	f	Solvent	Absorption [cm ⁻¹]	Emis [cn	Stokes shift [cm ⁻¹]	Φ
3	S₀ PLICT PLATICT	1.32 6.71 8.48	39100 28000 21400	11100 17700	0.045 0.107 0.0000003	<i>n</i> -hexane 1-chlorobutane dioxane acetonitrile	37200 36900 36800 36000	272 262 258 248	10000 10700 10900 11100	0.13 0.20 0.30 0.27
4	S₀ PLICT PLATICT	1.78 5.03 9.96	37600 28100 21800	9500 15800	0.042 0.095 0.000023	<i>n</i> -hexane 1-chlorobutane dioxane acetonitrile	37500 37000 36800 35600	274 262 257 248	10100 10800 11100 10800	0.10 0.13 0.15 0.11
5	S₀ PLATICT	1.25 14.07	38800 20100	18700	0.015 0.000012	<i>n</i> -hexane 1-chlorobutane dioxane	37300 36900 36500	22ť 192 18ť	14800 17700 17900	0.02 0.0003 0.0001
6	S₀ PLATICT	5.26 16.63	38300 19300	19000	0.022 0.000009	<i>n</i> -hexane 1-chlorobutane dioxane	38000 37600 37300	22: 19 ² 192	15700 18200 18100	0.02 0.0006 0.0004

For the PLATICT states, the change in the permanent dipole moments is even more pronounced than for the PLICT states: The permanent dipole moment of the PLICT state of **3** is 6.7 D; for the PLATICT state a value of 8.5 D is calculated. In the case of the PLATICT state of **6**, the permanent dipole moment has a value of even 16.6 D (Table 1). It is also interesting to compare the relative energies of the PLICT and PLATICT states of the 1-aminoindoles **3** and **4** (Table S2). If the B3LYP-optimized structures are used for the CC2 calculations, the PLATICT states are energetically preferred by ca. 6 kcal/mol. However, if the cam-B3LYP-optimized structures are taken, the PLATICT states of **3** and **4** are slightly energetically disfavored by 1-2 kcal/mol (Table S2). Hence, according to the CC2 calculations, both states can be formed for the aminoindoles **3** and **4**.

In Figure 5, the dominant natural transition orbital (NTO) pairs^[30] of the optimized PLICT state of **3** and of the PLATICT states of **3** and **6** calculated by means of cam-B3LYP are shown. The depicted orbitals can be considered as those orbitals which are occupied by the two unpaired electrons of the singlet diradical. The transition from S_1 to S_0 corresponds to a transition of an electron from the virtual to the occupied natural transition orbital. As the emissions are dominated by LUMO \rightarrow HOMO transitions, the dominant natural transition orbital pairs resemble the corresponding HOMOs and LUMOs (Figure S2).

In Table 1 the vertical emission ($S_0 \leftarrow S_1$) energies, the Stokes shifts and the oscillator strengths of each state calculated by means of CC2/def2-TZVP//TD-cam-B3LYP/def2-TZVP are listed. Furthermore, in Table S2 the Stokes shifts computed using different approximations are given. A comparison shows that the TD-B3LYP values of **3** and **4** strongly differ from the values obtained by cam-TD-B3LYP and CC2. This is properly due to the fact that TD-B3LYP overestimate the stabilization of charge transfer excitation states.^[25] The data from the TD-cam-B3LYP calculations agree well with those from the CC2//TD-cam-B3LYP approximation. The deviation of the CC2 values calculated on different geometries (TD-B3LYP and TD-cam-B3LYP) is small; this means that also the optimization using TD-B3LYP with subsequent CC2 single point calculation leads to reliable results for the Stokes shifts (Table S2).

The calculated (TD-cam-B3LYP and CC2) Stokes shifts of the PLICT states range between 9000 and 11000 cm⁻¹. Having oscillator strengths of about 0.1, the PLICT states can be regarded as electronically allowed transitions (Table 1). This is also evident, when the corresponding natural transition orbitals of **3** are considered (Figure 5a). As both orbitals are located in the same plane, the π systems are coupled and the resulting fluorescence is electronically allowed.

Due to the independent rotations around two different axes, the calculated (CC2) Stokes shifts of the PLATICT states are very large (14000 to 19000 cm⁻¹; see Tables 1 and S2). As the rotation around the dihedral angle θ_2 (N1-N8-C9-C10) leads to orbitally decoupled π

systems, whereby one electron is located in the 1-aminoindole system (occupied NTO) and the other one in the phenyl ring (virtual NTO) being perpendicular to the 1-aminoindole system (Figures 5 and S3). The orbitally decoupled π systems lead to the fact that the emission to the ground state is electric dipole forbidden resulting in very low fluorescence quantum yields.



Figure 5. Occupied (lower panel) and virtual (upper panel) natural transition orbitals of the optimized PLICT state of **3** (a) and of the PLATICT states of **3** (b) and **6** (c) calculated by means of cam-B3LYP.

c) Experimental Investigation of the PLATICT States

To examine the above concept and the corresponding quantum chemical calculations, we synthesized the 1-aminoindoles **3-6** and investigated their spectroscopic properties. The synthesis of **3-6** were conducted by the treatment of indoline (**7**) with the corresponding nitroso compound **8-11** in the presence of benzoic acid in toluene as solvent (Scheme 1). The 1-aminoindoles **3-6** could be isolated in yields of 46-70%. Prior to the fluorescence measurements, the 1-aminoindoles **3-6** were crystallized twice from a mixture of *n*-hexane and tetrahydrofuran. The fluorescence spectra were recorded in the solvents *n*-hexane, 1-chlorobutane, dioxane and acetonitrile (Figures 6 and S5-S7). The experimentally determined spectral properties of the aminoindoles **3-6** are also listed in Table 1.



Scheme 1. Synthesis of the aminoindoles 3-6 (46-70% yield) starting from indoline (7) and the nitroso compounds 8-11.





If the experimentally determined Stokes shifts and the fluorescence quantum yields are considered, it can be noticed two different types (Table 1, Figures 6 and S5-S7). The 1-aminoindoles **3** and **4** belongs to the first type showing Stokes shifts in the range from 10000 to 11000 cm⁻¹ (100-120 nm) and fluorescence quantum yields of about 0.1 to 0.3. Let's consider as comparison the fluorophores indole and 1-aminoindole. In the case of indole, no rotation relaxation can occur in the excited state and accordingly the Stokes shift has only a value of about 5000 cm⁻¹ in cyclohexane.^[31] 1-Aminoindole (**2**) is a pure PLICT compound and exhibits a Stokes shift of 9300 cm⁻¹ in cyclohexane.^[10] Hence, the recorded Stokes shifts of **3** and **4** in the range from 10000 to 11000 cm⁻¹ corresponds to the transition from the PLICT state to the ground state. A comparison of the calculated (CC2//TD-cam-B3LYP) and 12

experimentally determined Stokes Shift shows a good match between calculation and experiment (Tables 1 and S2). As predicted by the CC2//TD-cam-B3LYP computations, only the 1-aminoindoles **3** and **4** have PLICT states as minima on the energy surface and these PLICT states are energetically more stable than the PLATICT states. The emission from the PLICT states is allowed and the bands are red-shifted with increasing polarity of the solvents (Table 1). This underpins the higher dipole moment of the excited state. The fluorescence quantum yields for the PLICT states are only marginally influenced by the polarity of the used solvents.

The second type of emission is found for the 1-aminoindoles 5 and 6. The bands show very large Stokes shifts ranging from 15000 to 18000 cm⁻¹ (180-260 nm) as well as fluorescence quantum yields being lower than 0.02. The quantum yields strongly depend on the polarity of the used solvents. The higher the polarity of the solvent is, the lower are the quantum yields. In acetonitrile as solvent, fluorescence cannot be observed neither for 5 nor for 6. The low fluorescence quantum yields and their dependence on the solvent indicate that the corresponding transitions are forbidden ones.^[23] As comparison let us consider the fluorescence spectra of the TICT compound DMABN (1). In n-hexane as solvent, only the "normal" band showing a Stokes shift of 6200 cm⁻¹ can be recorded (Figure S3). In the medium polar, aprotic solvent 1-chlorobutane an emission band from the TICT state can be observed as a shoulder of the "normal" band (Figure S3).^[5,4] The Stokes shift of this TICT band amounts to about 9800 cm⁻¹. Opposite to this, the emission bands of **5** and **6** show even in *n*-hexane very large Stokes shifts (ca. 15000 cm⁻¹) and in 1-chlorobutane their values are higher by ca. 8000 cm⁻¹ than that measured for DMABN. This allows the conclusion that the recorded emission bands of 5 and 6 stem from PLATICT states, and not from PLICT or TICT states. As expected for the highly polar PLATICT states, the magnitude of the Stokes shifts and fluorescence quantum yields strongly depends on the polarity of the solvent.

A comparison of the calculated (CC2//TD-cam-B3LYP) und experimentally recorded Stokes Shift of the PLATICT states shows a fairly good match between calculation and experiment (Table 1), whereby the calculated values are slightly higher than the experimental observed ones.

Conclusion

In sum, we could show by means of quantum chemical calculations (TD-cam-B3LYP and CC2) that *N*-aryl-substituted 1-aminoindoles can form photoinduced **pl**anarized **a**nd **t**wisted intramolecular **c**harge **t**ransfer (PLATICT) states. These states are an amalgamation of the well-known TICT and the previous reported PLICT states. The investigated *N*-aryl-substituted 1-aminoindoles show both a TICT and a PLICT unit, whereby one nitrogen atom belongs to both systems. The intramolecular charge transfer causes both a twisting around one single

bond and a planarization around another one. In sum, the PLATICT system shows two independent rotations around different axes in the excited state. The experimentally determined absorption and fluorescence spectra of the *N*-aryl-substituted 1-aminoindoles confirm the quantum chemical predictions: *N*-aryl-substituted 1-aminoindoles with a methoxycarbonyl or a cyano group as substituent in the aryl ring show emission bands which stem from the PLATICT states. Due to two rotations in the excited state, these bands have very large Stokes shifts (>250 nm; >18000 cm⁻¹). As *N*-aryl-substituted 1-aminoindoles can be easily synthesized from indoline, they are attractive candidates both for optical switches and for molecular machines.

Experimental Section

Computational Details

All calculations were performed by using the program packages TURBOMOLE^[32] and Gaussian 09^[33]. The geometrical parameters of the electronically ground states were optimized by means of B3LYP^[18] and cam-B3LYP^[25]. The optimized geometries of the excited states were obtained on the basis of time-dependent density functional theory (TD-DFT)^[19] with the functionals B3LYP and cam-B3LYP. The def2-TZVP^[26] basis set was employed for both functionals. To optimize the geometric parameters of the excited states S_1 by means of cam-B3LYP/def2-TZVP, the five energetically lowest excited singlet states were solved in each step and the lowest of them were used for optimization. In order to locate the minima of the excited states S_1 , starting geometries structures with different dihedral angles θ_1 and θ_2 were used. For all stationary points no symmetry restriction was applied. Frequency calculations were carried out at each of the structures to verify the nature of the stationary point. All optimized states have none imaginary frequency. Furthermore, the energies, the electronic excitation energies, the permanent dipole moments and the oscillator strengths for the transitions were computed at the approximate second-order coupled cluster (CC2^{[27],[28]}) levels on the B3LYP- and cam-B3LYP-optimized structures. Here again def2-TZVP^[26] was used.

General remarks: All chemicals were reagent grade and were used as purchased. Reactions were monitored by TLC analysis with silica gel 60 F254 thin-layer plates. Flash chromatography was carried out on silica gel 60 (230-400 mesh). ¹H and ¹³C NMR spectra were recorded on a 600 MHz spectrometer. All chemical shifts (δ) are given in ppm. The spectra were referenced to the peak for the protium impurity in the deuterated solvents indicated in brackets in the analytical data. HR-MS spectra were recorded using a time of flight (TOF) detector. The 1-aminoindoles were synthesized starting from indoline (**7**) and the nitrosobenzene derivatives **8-11** in analogy to a known procedure.^[34] The nitrosobenzene derivatives **8-11** were either purchased or prepared from the corresponding anilines.^[35] Prior

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to the fluorescence measurements, the 1-aminoindoles **3-6** were crystallized twice from a mixture of *n*-hexane and tetrahydrofuran.

General procedure: To a mixture of indoline (298 mg, 2.5 mmol) and benzoic acid (92 mg, 0.75 mmol) in dry toluene (5 mL), the nitrosobenzene derivative (2.5 mmol) in 4 mL dry toluene was added dropwise over 1 hour at 110 °C. After 1 h stirring at 110 °C, the reaction mixture was cooled to room temperature. The product was isolated by column chromatography over silica gel (*n*-hexane/ethyl acetate) to yield the 1-aminoindole as an off-white solid. The 1-aminoindole was further purified by crystallization from *n*-hexane/ tetrahydrofuran to give a white solid.

Aminoindole 3. Yield: 70%; M.p. 91-92 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.65 (d, ³*J*_{H,H} = 7.6 Hz, 1 H, *H*_{ar}), 7.29 (d, ³*J*_{H,H} = 8.2 Hz, 1 H, *H*_{ar}), 7.22-7.14 (m, 5 H, *H*_{ar}), 6.91 (t, ³*J*_{H,H} = 7.4 Hz, 1 H, *H*_{ar}), 6.64 (s, 1 H, N*H*), 6.55 (d, ³*J*_{H,H} = 3.3 Hz, 1 H, *H*_{ar}), 6.53 (d, ³*J*_{H,H} = 7.7 Hz, 2 H, *H*_{ar}) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 147.32, 135.82, 129.38, 128.63, 126.60, 122.43, 121.20, 121.08, 120.35, 112.69, 109.40, 100.85 ppm; IR (ATR): 3311, 3129, 3100, 3049, 3030, 1600, 1510, 1494, 1473, 1457, 1386, 1365, 1317, 1291, 1238, 1221, 1179, 1158, 1128, 1089, 1045, 1026, 1007, 929, 885, 870, 847, 801, 763, 743, 735, 688 cm⁻¹; HRMS (ESI+): *m/z* calcd for C₁₄H₁₂N₂+H⁺: 209.1079; found: 209.1081.

Aminoindole 4. Yield: 62%; M.p. 115-116 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.65 (d, ³J_{H,H} = 7.7 Hz, 1 H, H_{ar}), 7.26 (d, ³J_{H,H} = 7.4 Hz, 1 H, H_{ar}), 7.21-7.18 (m, 2 H, H_{ar}), 7.15 (dt, ³J_{H,H} = 7.5 Hz, ⁴J_{H,H} = 1.1 Hz, 1 H, H_{ar}), 6.92-6.88 (m, 2 H, H_{ar}), 6.58 (s, 1 H, NH), 6.54 (d, ³J_{H,H} = 3.3 Hz, 1 H, H_{ar}), 6.49-6.46 (m, 2 H, H_{ar}) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 158.00 (¹J_{C,F} = 239.0 Hz), 143.60, 135.83, 128.63, 126.82, 122.66, 121.33, 120.60, 116.13 (²J_{C,F} = 22.9 Hz), 114.11 (³J_{C,F} = 7.8 Hz), 109.46, 101.12 ppm; IR (ATR): 3331, 3137, 3056, 1867, 1605, 1503, 1473, 1455, 1391, 1367, 1328, 1316, 1298, 1245, 1224, 1208, 1155, 1126, 1102, 1090, 1045, 1006, 927, 881, 866, 823, 764, 748, 729 cm⁻¹; HRMS (ESI+): *m/z* calcd for C₁₄H₁₁FN₂+H⁺: 227.0985; found: 227.0975.

Aminoindole 5. Yield: 57%; M.p. 149-150 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.90-7.88 (m, 2 H, H_{ar}), 7.66 (d, ³ $J_{H,H}$ = 7.3 Hz, 1 H, H_{ar}), 7.24 (d, ³ $J_{H,H}$ = 8.2 Hz, 1 H, H_{ar}), 7.21-7.15 (m, 3 H, H_{ar}), 6.90 (s, 1 H, NH), 6.58 (d, ³ $J_{H,H}$ = 3.3 Hz, 1 H, H_{ar}), 6.52-6.50 (m, 2 H, H_{ar}), 3.86 (s, 3 H, OCH₃) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 166.73, 151.09, 135.58, 131.53, 128.32, 126.65, 122.75, 121.26, 120.71, 111.67, 109.18, 101.49, 51.81 ppm; IR (ATR): 3315, 3101, 3058, 2950, 1684, 1602, 1515, 1475, 1460, 1432, 1389, 1307, 1280, 1261, 1216, 1194, 1173, 1114, 1090, 1049, 1007, 967, 937, 881, 846, 798, 764, 740, 728, 698, 662 cm⁻¹; HRMS (ESI+): *m/z* calcd for C₁₆H₁₄N₂O₂+H⁺: 267.1134; found: 267.1133.

Aminoindole 6. Yield: 46%; M.p. 171-172 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.66 (dt, ³J_{H,H} = 7.4 Hz, ⁴J_{H,H} = 1.2 Hz, 1 H, H_{ar}), 7.48-7.46 (m, 2 H, H_{ar}), 7.22-7.16 (m, 3 H, H_{ar}), 7.15 (d, ³J_{H,H} = 3.4 Hz, 1 H, H_{ar}), 6.98 (s, 1 H, NH), 6.59 (d, ³J_{H,H} = 3.4 Hz, 1 H, H_{ar}), 6.53-6.50 (m, 2

H, H_{ar}) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 150.69, 135.36, 133.89, 128.02, 126.68, 122.96, 121.40, 120.94, 119.28, 112.35, 108.99, 103.68, 101.93 ppm; IR (ATR): 3323, 3132, 3105, 3057, 2215, 1604, 1518, 1510, 1472, 1456, 1417, 1394, 1370, 1324, 1304, 1261, 1222, 1173, 1130, 1090, 1051, 1007, 967, 957, 932, 882, 849, 825, 762, 747 717 cm⁻¹; HRMS (ESI+): m/z calcd for C₁₅H₁₁N₃+H⁺: 234.1031; found: 234.1032.

Supporting Information

NMR spectra of **3-6**, calculated properties, absorption and fluorescence spectra, cartesian coordinates and absolute energies for all calculated compounds.

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