Probing the Aggregation and Signaling Behavior of Some Twisted 9,9’-Bianthryl Derivatives: Observation of Aggregation-Induced Blue-Shifted Emission

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Supporting Information

ABSTRACT: With an aim to understand the photophysical behavior of twisted organic fluorescent molecules in their aggregated state, two twisted biaryl molecules, namely, 9,9’-bianthryl and 10,10’-dicyno-9,9’-bianthryl, have been synthesized and characterized by conventional spectroscopic methods. To understand the role of C–C bond twisting on the photophysical response of biaryl aggregates, monoaryl counterparts (anthracene and 9-anthracenecarbonitrile) of the biaryl systems are also investigated. Photophysical behaviors of these systems along with their monoaryl counterpart are investigated in both solution and aggregated state. Investigations reveal that fluorescence spectra of the biaryl compounds show blue-shifted emission upon aggregation. Interestingly, no blue shift of the emission has been observed for monoaryl aggregates. Photophysical data of biaryl systems compared to monoaryl unit reveal that change in geometry, during self-assembly process, disfavors the formation of charge-transfer state, which eventually causes blue shift in the emission upon aggregation. In addition to this, potential of these systems toward signaling of nitroaromatic explosive has also been explored. Among all of the nitroaromatics, the highest fluorescence quenching is observed for nitrophenols (say picric acid (PA)). The investigation also reveals that compared to monoaryl systems, biaryl systems are more responsive to fluorescence quenching by nitroaromatics. Perrin’s model of quenching sphere action has been attributed to nitrophenol (PA) selective signaling behavior of biaryl systems.

1. INTRODUCTION

In recent times, both organic and inorganic solid-state luminescent materials have attracted considerable attention as they have potential to be used in display, optoelectronic devices, sensor applications, etc. 1-4 Among these, organic nanoparticles have certain advantages over inorganic ones in optoelectronic devices function in solid state, 7 workers 18,19 have developed some silole-based organic material can be very desirable and developed.

The photophysical behavior of an aggregated solid-state material can be very different from its monomeric form in solution state. Different structural arrangement and intermolecular interaction in solid-state material (compared to the monomeric form) can lead to changes in the optical behavior of these systems. 9,11-13 Organic molecules usually upon aggregation exhibit red shift in the absorption and emission spectra. 14 Molecules upon aggregation usually also cause quenching of fluorescence. 15-17 Recently, Tang and coworkers 18,19 have developed some silole-based organic fluorophore molecules, which show aggregation-induced emission property. We note that blue shift in the emission spectrum upon aggregation is an uncommon phenomenon. Observation of blue-shifted emission upon aggregation is very interesting and is known as aggregation-induced blue-shifted emission (AIBSE). 20-23 It has been shown by Yang and co-workers 24-26 that several substituted anthracene (AN) molecules at the 9,10-positions in solid state can also exhibit blue-shifted emission band. However, aggregation-induced red-shifted emission is attributed to factors such as (1) excitonic coupling, (2) increase in charge transfer (CT) character due to geometry change, (3) J-aggregate formation, and (4) change in the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap. 27a-c The underlying mechanism for AIBSE is still hazy. Only few studies have been carried out on this aspect. It is also noteworthy to mention in this context that a recent study based on quantum mechanical calculation (quantum mechanics/molecular mechanics (QM/MM)) has shown that lower reorganization energy in aggregate compared to the solution can also cause a blue-shifted emission band. 28 The above discussion tells us
that studies, particularly experimental studies, which are focused on understanding the mechanism of AIBSE process are rather limited. Outcomes of such studies are expected to be useful as they provide clue to tune the optical properties of organic aggregates.

In this context, molecules having twisted structure that possess two anthracene rings connected through C–C bond could be an interesting research target. Photophysical studies on these systems in their molecular and aggregated forms are expected to provide valuable information on structure–optical property correlation, which, in turn, may be useful to understand photoprocesses such as AIBSE. Note that it has been well established that twisted biaryl system exhibits some interesting photophysical behavior. Several studies have explored the excited-state behavior and dynamical processes of biaryl derivatives. One such interesting system is 9,9′-bianthryl (BA), as this molecule in the ground state contains two mutually perpendicular anthracene rings connected through C–C bond. It undergoes symmetry breaking upon excitation, and its fluorescence spectra show a distinct charge transfer (CT) character, especially in the polar solvents. Although extensive studies on molecular forms of biantartic systems have been done by several research groups, the photophysical behavior of these systems in aggregated state has not been studied.

Since biantartic derivatives having conjugated electronic π-clouds have some interesting optical properties, such as high quantum yield (QY), good photostability, etc., they are suitable for fluorescence signaling behavior. Moreover, organic fluorophores having extended π-cloud are known to be quite useful for the detection of nitroaromatics (NACs). We have also explored the BA system for signaling of nitroaromatics. Additionally, we have also tried to understand the mechanism of fluorescence signaling behavior of the BA system toward nitroaromatics.

Considering the above-mentioned facts, in the present study, we have synthesized two twisted molecules, namely, 9,9′-bianthryl (BA) and 10,10′-dicyano-9,9′-bianthryl (DCBA), and investigated the photophysical behaviors of these two fluorescent molecules, in both molecular and aggregated forms, and the obtained data are compared to those of their monomeric unit anthracene (AN) and 9-anthracenecarbonitrile (CA), respectively (Chart 1). Photophysical data reveal that only biantartic systems exhibit a blue shift in the emission upon aggregation, whereas monoaryl systems do not. The observation indicates that change in geometry of the concerned biantartic derivatives during the self-assembly process could be responsible for AIBSE process.

During the signaling event, fluorescence response of biantartic systems in the presence of nitroaromatics is observed to be different from that observed for monoaryl systems. Both biantartic systems (BA and DCBA) exhibit high selectivity toward nitrophenols. The “sphere of action” quenching mechanism is found to be primarily responsible for the nitrophenol (picric acid (PA)) signaling event. The present study reveals that biantartic systems can effectively be used for the detection of explosive nitroaromatics.

2. RESULTS AND DISCUSSION

9,9′-Bianthryl (BA), 10,10′-dicyano-9,9′-bianthryl (DCBA), and their respective monomeric counterparts, namely, anthracene (AN) and 9-anthracenecarbonitrile (CA), are investigated in both molecular and aggregated forms using steady-state absorption, emission, and time-resolved fluorescence studies.

2.1. Photophysical Behaviors of AN, BA, CA, and DCBA in Molecular Form. Before studying the aggregation behavior of BA systems, we have studied the photophysical behavior of AN, BA, CA, and DCBA in their molecular form in some selected solvents of varying polarity. The representative absorption spectra of BA and DCBA are shown in Figure 1. The corresponding absorption spectra of AN and CA are shown in Figure S1 (Supporting Information). From Figures 1 and S1, it can be observed that the vibrational structure and peak position of the absorption band of all of the four compounds do not change much with change in the polarity of solvent from nonpolar cyclohexane to polar acetonitrile. The similarity in the nature of the spectra of the biantartic compounds (BA and DCBA) in the ground state to that of only anthracene moiety indicates that the origin of absorption is mainly π−π* transition in all cases. These data also show that in the ground state, two anthracene units of biantartic systems are electronically decoupled as they remain in mutually perpendicular orientation.

The emission spectra for all of the present monoaryl and biantartic systems (AN, CA, BA, and DCBA) in some selected solvents are shown in Figure 2. The data corresponding to absorption and emission maxima of the compounds in some selected solvents are listed in Table 1. Unlike absorption spectra of the above compounds, which do not depend much on solvent polarity, the fluorescence spectra of these compounds are observed to be highly dependent on solvent polarity. It can be seen from Figure 2 that with increase in the polarity of solvents, the fluorescence spectra become broadened and show considerable red shift of emission band. Interestingly, one can also see from Figure 2 and Table 1 that as we move from nonpolar cyclohexane to polar acetonitrile, the extent of red shift in the emission maxima is much higher for biantartic systems than for their parent monomeric units. For example, upon going from cyclohexane to acetonitrile, BA shows a 57 nm red shift in the emission, whereas AN shows only a 6 nm red shift. Also DCBA shows a 72 nm red shift in the emission maxima as we move from nonpolar cyclohexane to polar acetonitrile, whereas its monomeric unit CA shows a 21 nm red shift. Schneider and Lipert previously observed the solvent-polarity-dependent emission behavior of biantartic systems. Both broadening and red shift of emission spectra for biantartic systems with increasing the polarity of solvents indicate the formation of charge transfer (CT) state in

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**Chart 1. Molecular Diagrams of Anthracene (AN), 9-Anthracenecarbonitrile (CA), 9,9′-Bianthryl (BA), and 10,10′-Dicyano-9,9′-bianthryl (DCBA)**

[Diagram of molecular structures]
the polar media upon excitation. Interestingly, when we compare the fluorescence spectra of all monoaryl and biaryl systems in a given solvent dimethyl sulfoxide (DMSO) (Figure 3), fluorescence spectra of biaryl systems are observed to be broadened (structureless) and more red-shifted compared to their respective monoaryl systems. This observation clearly suggests that in a polar solvent, biaryl systems emit from the polar CT state.

It is pertinent to mention in this context that the fluorescence of BA and its derivative are strongly dependent on the polarity of the solvent and are linked to two different excited states, namely, a locally excited (LE) state and an intramolecular charge transfer (CT) state. Several research groups have studied the nature of the emitting states for BA systems. Iwakura and co-workers depicted that in polar solvents, the CT state predominates, which is formed
from the LE state by one-electron oxidation–reduction of the two anthracene rings. Warman and co-workers demonstrated that an unstable CT state induces a rapid flip-flop of dipole between two anthracene rings and remains in LE state in nonpolar solvent. Some of the recent studies on bianthryl derivatives have also revealed that the CT state originates from the LE state and there exists an equilibrium between the exchange process of the LE and CT states at the picosecond scale depending on the solvent polarity.

2.2. Photophysical Behavior of AN, BA, CA, and DCBA in Aggregated Form.

UV–vis absorption and fluorescence studies on the well-characterized aggregates of AN, BA, CA, and DCBA have been carried out and the obtained results are compared to those in their respective molecular form. The absorption spectra of biaryl systems, BA and DCBA, in their molecular and aggregated forms are provided in Figure 4. The absorption spectra for monoaryl systems, AN and CA, are also provided in the Supporting Information (Figure S2). As can be seen from the absorption spectra, the absorption maxima of all the compounds in aggregated form are red-shifted compared to those in their molecular form. Photophysical data corresponding to the absorption behavior of monoaryl and biaryl systems in their molecular and aggregated forms are provided in Table 2. Interestingly, we have also observed that the shift in the absorption maximum upon aggregation is less for biaryl systems (BA and DCBA) than for their respective monomeric counterparts (AN and CA). For example, in the case of biaryl systems, the extents of red shift in the absorption maximum of BA and DCBA aggregates are 8 and 18 nm, respectively.

**Table 1. Absorption and Emission Maxima of AN, BA, CA, and DCBA in Solvents with Varying Polarity**

| solvents *a* | AN | BA | CA | DCBA |
|--------------|----|----|----|------|
| cyclohexane (30.9) | λ<sub>max</sub> (nm) | 376 | 399 | 389 | 414 | 378 | 428 | 413 | 439 |
| toluene (33.9) | 378 | 403 | 392 | 418 | 383 | 437 | 417 | 449 |
| dichloromethane (DCM, 41.1) | 378 | 403 | 391 | 448 | 383 | 440 | 417 | 458 |
| tetrahydrofuran (THF, 37.4) | 377 | 401 | 390 | 433 | 382 | 437 | 416 | 459 |
| acetonitrile (45.6) | 375 | 401 | 389 | 467 | 381 | 440 | 414 | 498 |
| DMSO (45.0) | 380 | 405 | 393 | 473 | 388 | 449 | 420 | 511 |

*a* In parentheses, solvent polarity parameter E<sub>T</sub> (30) values are given from ref 42.

**Figure 3.** Normalized fluorescence spectra of 2 × 10<sup>−6</sup> M solutions of AN (blue), BA (black), CA (green), and DCBA (red) in DMSO at λ<sub>exc</sub> = 375 nm.

**Figure 4.** Normalized absorption spectra of (a) BA in molecular form (2 × 10<sup>−6</sup> M solution in DMSO) and aggregated form (water–DMSO mixture) and (b) DCBA in molecular form (2 × 10<sup>−6</sup> M solution in DMSO) and aggregated form (water–DMSO mixture). λ<sub>exc</sub> = 375 nm.
respectively, whereas monoaryl systems, AN and CA, show 19 and 38 nm red shift, respectively, in absorption maxima upon aggregation (Table 2).

This larger red shift in the aggregated state of monoaryl systems (AN and CA) can be attributed to relatively more lowering of the HOMO–LUMO energy gap in the aggregates of monoaryl systems.\(^{55,56}\) This is indicative of better electronic coupling between the smaller molecules (AN and CA) in the aggregated state compared to that of relatively larger BA and DCBA.\(^{55,56}\) The absorption, emission maxima, fluorescence lifetime, and quantum yield values of the concerned systems in both molecular and aggregated forms are provided in Table 2.

To confirm that the shift in the absorption maxima of the concerned systems upon aggregation (in DMSO–water mixture) is not due to the solvent polarity-induced change of monomeric molecules, we have recorded the absorption spectra of the compounds in methanol–water system, whose polarity is maintained close to that of the DMSO–water system. The shift in the absorption maxima of the molecules in methanol–water system is found to be less (ca. 2 nm) in all cases compared to that observed for the present aggregates (in DMSO–water system). This observation confirms that this red shift in the absorption maxima is due to the J-aggregation of the particles and not due to the change in solvent polarity. As stated in Experimental Section (vide infra), the formation of aggregates is also confirmed through dynamic light scattering (DLS) and field emission scanning electron microscopy (FESEM) studies. Also note that the appearance of long tail absorbance for the aggregates at the longer wavelength region (at around 450–500 nm) indicates the Mie-scattering effect,\(^{57,58}\) which is also indicative of the formation of a strongly coupled aggregated system.

The excited state of the aggregates is investigated by exploiting steady-state and time-resolved fluorescence spectroscopy. Figure 5 shows the emission spectra of BA and DCBA aggregates along with their monomeric form. The emission spectra for monoaryl systems (AN and CA) in their molecular and aggregated forms are provided in the Supporting Information (Figure S3). It can be seen that like absorption, the emission maxima of aggregates of monoaryl systems (AN, CN) are red-shifted compared to their respective monomeric form. However, more interestingly, for biaryl systems (BA and DCBA), upon aggregation, a blue shift in the emission maximum of the aggregates compared to their respective monomeric form is observed (Figure 5). This blue-shifted emission in the present case is an interesting observation, as red shift in the emission spectra with quenching of fluorescence intensity upon aggregation is a very common phenomenon, but blue shift of emission due to the formation of aggregates with quenching of fluorescence intensity is uncommon. This process is known as the aggregation-induced blue-shifted emission (AIBSE) phenomenon.\(^{18,20,21,59–65}\) Even though the observation of the AIBSE phenomenon is quite interesting, the actual reason behind this process is still unclear. Upon a careful look at Figure 5, one can also see that upon aggregation, the emission spectral profiles of the aggregates become more structured compared to their monomeric form. The appearance of structured (less broadened) emission band upon aggregation perhaps also arises due to the reduction in the solute–solvent interaction as the solvent molecules will be dislodged from the surrounding of the BA system during the self-assembly of two aromatic moieties. To confirm the aggregation-induced quenching of fluorescence intensity for the aggregates, we have studied the concentration-dependent fluorescence properties of the biaryl systems (Figure 6). It has been found that on increasing the concentration of both BA and DCBA solutions from \(10^{-5}\) to \(10^{-4}\) M, a sharp increase in the emission intensity of the solutions occurs. Interestingly, upon further increase in the concentration of the biaryl systems

| systems     | \(\lambda_{\text{abs}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\tau_f\) (ns) | \(\phi_f\) |
|-------------|-------------------------------|-----------------------------|-----------------|----------|
| AN molecule | 380                           | 405                         | 3.3             | 0.20     |
| AN aggregate| 399                           | 418                         | 2.0             | 0.12     |
| BA molecule | 393                           | 471                         | 30.1            | 0.25     |
| BA aggregate| 401                           | 459                         | 0.7             | 0.09     |
| CA molecule | 388                           | 449                         | 14.9            | 0.75     |
| CA aggregate| 426                           | 494                         | 10.0            | 0.42     |
| DCBA molecule| 420                          | 511                         | 19.9            | 0.18     |
| DCBA aggregate| 438                         | 509                         | 2.9             | 0.04     |

\(^{a}\)\(\lambda_{\text{exc}} = 375\) nm.

Figure 5. Emission spectra of (a) BA and (b) DCBA in molecular form of \(2 \times 10^{-5}\) M solution in DMSO (black) and aggregated form in DMSO–water mixture (red). The inset provides the normalized emission spectra of BA and DCBA in its molecular and aggregated states at \(\lambda_{\text{exc}} = 375\) nm.
(5 × 10^{-4} and 10^{-3} M), the fluorescence intensity of the solutions is observed to decrease significantly for both the systems. This significant quenching of fluorescence of BA and DCBA systems at higher concentration clearly proves that the aggregation-induced quenching process is primarily responsible for the quenching of fluorescence of the concerned systems upon aggregation. Note that similar arguments have also been provided by Yang and co-workers in the case of aggregation-induced quenching study of bis[2-(9-anthracenyl)vinyl]benzene.

The emission spectra of the two compounds in the DMSO and DMSO/H2O mixture with increasing water content have also been recorded. From Figure 7, we can say that with increasing the volume percentage of water up to 80% in the DMSO solutions of BA and DCBA, the fluorescence intensities of the aggregates are found to decrease about 25.8 and 24.2 times, respectively, with a concomitant shift of the emission maxima toward the shorter (blue) wavelength region. From this observation, it can be clearly said that addition of a large volume of water induces aggregation.

Note that in the present study, this blue-shifted emission occurs only in C–C bond containing biaryl systems, not in monoaryl systems, where C–C bond is absent. Therefore, this observation certainly indicates that in biaryl systems, C–C bond, which holds the two aryl ring together, plays an important role in determining the photophysical properties of these systems in the aggregated state. Previous studies have demonstrated that in the solid state of biaryl systems, two anthracene moieties remain in mutually perpendicular position. It has also been demonstrated that in a polar medium, emission of BA system takes place from a twisted intramolecular charge transfer (TICT) state, where two rings of bianthryl systems remain in a somewhat planar (non-perpendicular) conformation and the angle between the two rings of BA and DCBA becomes nearly 60°. Now, if during the aggregation process the biaryl systems somehow attain a geometry that disfavors the formation of TICT state through restricted rotation around central C–C bond, then this (restricted C–C bond rotation due to geometry change upon aggregation) could be one of the probable reasons for which BA and DCBA upon aggregation can exhibit a blue-shifted emission.

It is pertinent to mention here that recently Shuai and co-workers have studied the aggregation behaviors of three organic molecules, namely, 9,10-distrylanthracene, 2,3-dicyano-5,6-diphenylpyrazine, and cis,cis-1,2,3,4-tetraphenyl-1,3-butadiene through theoretical (QM/MM) studies and made an attempt to understand the AIBSE phenomenon. During the study, they stated that change in solvent reorganization energy from solution to solid state and freezing of low-frequency
vibrational modes in aggregated state can cause AIBSE. However, we would like to stress here that since no blue shift in the emission of the aggregates of monoaryl systems AN and CA is observed in the present study (Figure S3), we can say that in the case of BA and DCBA aggregates, geometric restriction (due to aggregation) plays a more important role in the AIBSE behavior rather than in the freezing of low-frequency vibration mode. Interestingly, when we compare the emission spectra of the bianthryl derivatives in solution with the solid-state emission (Figure S4), it is found that the emission of BA in solid state is blue-shifted compared to that of BA in solution phase.

Figure 8. (a) Molecular structure and (b) crystal packing of BA from single-crystal X-ray analysis (crystal structure taken from ref 69, CCDC 123938). H atoms except those involved in C−H⋯π interaction are omitted for clarity.

Figure 9. Absorption spectra of AN (12 μM) in the presence of 24 μM solution of (a) DNP and (b) DNT and absorption spectra of BA (12 μM) in the presence of 24 μM solution of (c) DNP and (d) DNT. The inset in (c) shows the absorption of only DNP in DMSO.
Here, we note that organic nano-/microcrystals usually formed due to the self-assembly of individual monomeric units and the structure property correlation of such systems can be realized by following the gradual evolution of crystal from a nanoscopic site domain to microcrystalline and bulk solid.\(^{67,68}\) Therefore, when we look at the optical output signals of solution, colloid, and solid forms of present biaryl and monoaryl systems, we can perhaps say that in colloidal state, these systems attain a twisted geometry (dihedral angle \(\sim 90^\circ\)), where CT transition is not favorable, and consequently due to this reason, for BA systems, a blue-shifted emission upon aggregation is observed. Therefore, the present study points out that the change in geometry during the self-assembly process can also be an important factor causing the AIBSE process.

Time-resolved fluorescence measurement reveals that upon aggregation, lifetime values (from Table 2) decrease for both monoaryl and biaryl systems. The representative fluorescence intensity decay profiles of both monoaryl and biaryl systems in molecular and aggregated states are provided in Figure S5. To throw more light on the fluorescence quenching process of the aggregates, we have calculated the nonradiative decay rate constants corresponding to the aggregates and their respective monomers using the equation \(k_{nr} = (1 - \phi_f)/\tau_f\) where \(k_{nr}\) is the nonradiative rate constant, \(\phi_f\) is the quantum yield, and \(\tau_f\) is the fluorescence lifetime. The nonradiative decay rate constants for BA and DCBA in molecular form are obtained as \(2.5 \times 10^7\) and \(4.1 \times 10^7\) s\(^{-1}\), whereas those for aggregated state are obtained as \(1.3 \times 10^7\) and \(3.3 \times 10^7\) s\(^{-1}\), respectively. Similarly, the nonradiative decay rate constants for AN and CA in molecular form are obtained as \(2.4 \times 10^8\) and \(1.7 \times 10^8\) s\(^{-1}\), whereas those for aggregated state are obtained as \(4.4 \times 10^8\) and \(5.8 \times 10^8\) s\(^{-1}\), respectively. The decrease in fluorescence lifetime in aggregated state compared to monomeric form can be attributed to the aggregation-induced quenching of the excited states, which, in turn, occurs because of increase in the nonradiative decay pathways in the aggregated state.\(^{69,70}\)

2.3. Crystallographic Analysis of BA System. To understand the aggregation behavior of biaryl systems better, we have analyzed the packing of BA molecules in its crystal structure. The crystal structure of BA (CCDC 123938) was reported by Bell and Waring.\(^{71}\) The space group reported for the given crystal is \(P2_1/n\) (monoclinic). From the packing diagram of BA molecule (Figure 8), it can be realized that the molecules in the solid state are self-assembled primarily through C–H...π interactions. The intramolecular C–H...π interactions (C2–H2–π, 2.969 Å; C19–H19–π, 2.988 Å), observed in the crystal packing of BA molecules, are shown by the dotted red line (Figure 8). From these, it is now reasonable to assume that the colloidal aggregates of BA molecules are also formed through the self-assembly of BA molecules mediated by C–H...π interactions. Similar arguments can be made for the structurally similar DCBA molecule.

2.4. Signaling Behavior for Nitroaromatics. We have further studied the signaling behavior of monoaryl and biaryl systems (AN, CA, BA, and DCBA) toward nitroaromatics. The signaling of nitroaromatics explosives has been carried out by gradually adding some of the well-known representatives of explosive molecules such as p-nitrotoluene (NT), 2,4-dinitrotoluene (DNT), nitrobenzene (NB), 4-nitrophenol (NP), 2,4-dinitrophenol (DNP) and picric acid (PA) to all monoaryl and biaryl systems independently. We have measured the steady-state absorption spectra for the monoaryl and biaryl systems in the presence of all of the quencher molecules by gradually adding them into the solutions of the studied fluorophore. Representative absorption spectra are provided in Figure 9.

It can be seen from Figure 9 that the absorbance of AN and BA increases in the presence of DNP and DNT. Note that the DNP alone exhibits absorption maxima at 430 nm (inset of Figure 9c). Therefore, the increase in optical density (OD) of AN and BA in the presence of DNP and the appearance of a new band at around 430 nm can be thought to arise due to the presence of DNP in the system. Similar observations have been found for other nitrophenol derivatives (PA and NP). The present data do not clearly indicate the ground-state complex formation. In the present case, interaction between the fluorophore and quencher molecule is likely nonspecific in nature.\(^{70}\) Cyano derivatives (CA and DCBA) have also exhibited a similar trend of the absorption profiles of the fluorophores in the presence of nitrophenol and nitrotoluene derivatives. Further, fluorescence responses of monoaryl (AN and CA) and biaryl (BA and DCBA) systems in the absence and presence of various nitroaromatic systems have been investigated by gradually adding nitroaromatics to the monoaryl and biaryl derivatives independently. During the titration, fluorescence quenching of all of the monoaryl and biaryl fluorophores has been observed. However, the extent of

**Figure 10.** Fluorescence spectra of (a) BA and (b) DCBA (12 μM solution) in the presence of different nitroaromatics (24 μM solution) at \(\lambda_{exc} = 350\) and 375 nm, respectively.
fluorescence quenching is observed to be different for different quenchers. Figure 10 represents the fluorescence quenching of biaryl systems (BA and DCBA) in the presence of different nitroaromatics. For better comparison, the fluorescence quenching events for BA and DCBA with various nitroaromatics are shown in a bar diagram (Figure 11). The similar bar diagram for fluorescence quenching events of monoaryl systems (AN and CA) in the presence of different nitroaromatics is provided in Figure S6. From Figure 10, it can be said quite clearly that a significant quenching for both biaryl systems (BA and DCBA) has been observed in the presence of nitrophenol derivatives, whereas nitrotoluenes and nitrobenzene could not appreciably quench the fluorescence intensity of these systems. Note that greater quenching of

Figure 11. Percentage quenching efficiency of 12 μM solution of (a) BA and (b) DCBA in the presence of 24 μM solutions of different nitroaromatics.

Figure 12. UV–vis absorption spectra of 12 μM solution of sensor molecules (a) BA and (b) DCBA in the presence of 24 μM picric acid (PA).

Figure 13. Fluorescence titration of 12 μM solutions of (a) BA and (b) DCBA with increasing concentration (0–24 μM) of PA.
fluorescence for monoaryl system is also observed for nitrophenol derivatives than for other nitroaromatics employed in this study (Figure S6).

Another interesting aspect of this signaling study is that the extent of quenching of fluorescence intensity of monoaryl systems by nitroaromatic derivative (say PA) is significantly less compared to that of biaryl systems (Figures 11 and S6). Keeping the above observation in mind, the signaling behavior of the biaryl systems with nitrophenol derivatives is investigated further so as to understand the signaling mechanism of this quenching event.

Representative absorption spectra of BA and DCBA in the absence and presence of picric acid (PA) are shown in Figure 12. From the representative steady-state absorption spectra, it can be observed that the optical density (OD) of BA and DCBA increases in the entire range of concentration of PA. This is not surprising as nitrophenols such as PA and DNP themselves have absorption in that region.71 A similar observation in the absorption behavior of the BA and DCBA system has been made in the presence of other nitrophenol derivatives (DNP and NP).

The fluorescence titration experiments have also been carried out by taking BA and DCBA solutions independently with gradual addition of nitrophenol derivatives (PA, DNP, and NP). Fluorescence of BA and DCBA is found to be significantly quenched by all of the nitrophenol derivatives. The change in fluorescence spectra of BA and DCBA with PA is shown in Figure 13. The spectra corresponding to fluorescence titration of BA and DCBA with other nitrophenols (DNP and NP) are provided in Figure S7 (Supporting Information). Interestingly, the quenching of fluorescence intensity of BA and DCBA is found to be highest for PA. This fact can be more clearly realized by looking at the bar diagram (Figure 11), which also indicates the highest response for PA. Note that the signaling behavior of monoaryl systems (AN and CA) toward nitrophenols has also been studied (Figure S8). From Figure S8, it is evident that for monoaryl derivatives, the quenching efficiency is also highest for PA, followed by DNP. However, as stated earlier, for a particular quencher, fluorescence quenching is always found to be higher for biaryl systems than that for monoaryl systems.

To understand the quenching mechanism better, the fluorescence response of BA and DCBA in the presence of nitrophenol system has been analyzed further in the light of the classical Stern−Volmer (S−V) equation,70,72 which is shown below (eq 1).

\[
\frac{F_0}{F} = 1 + k_q [Q] = 1 + K_{SV}[Q]
\]

where \(F_0\) and \(F\) denote the fluorescence intensities before and after the addition of quencher \([Q]\), respectively, \(k_q\) is the bimolecular quenching constant, \(\tau_0\) is the lifetime of the fluorophore in the absence of quencher, \([Q]\) is the quencher concentration, and \(K_{SV}\) is the Stern−Volmer constant. Representative S−V plots for quenching of fluorescence intensity of BA and DCBA with nitrophenol derivatives are given in Figures 14 and 15. The classical S−V plots that are obtained for the fluorescence quenching event of both BA and DCBA with DNP and NP exhibit a linear correlation of \(F_0/F\) versus \([Q]\) data for the entire concentration range of the concerned quencher (Figure 14a,b). However, in the case of fluorescence quenching of BA and DCBA by PA, the S−V plot demonstrates a linear correlation of \(F_0/F\) versus \([Q]\) data up to a certain concentration level (ca. 10 μM) (Figure 15a,b).
Above this concentration limit, the $F_0/F$ versus $[Q]$ data suddenly show an upward deviation (Figure 15a,b). The linear $S-V$ plots in the case of DNP and NP indicate only one type of quenching process, i.e., either pure static or pure dynamic quenching, but the nonlinear $S-V$ plot (upward curvature toward $F_0/F$ axis) in the case of PA indicates that the quenching mechanism is entirely different from the other quenchers and both static and dynamic quenching processes can be operational during the quenching event. Note that in the absence of dynamic quenching, the upward curvature in the classical $S-V$ plot that has been observed for PA system in the present study can also be explained by employing static quenching with “sphere of action” model. In this context, it may be noted that the measurement of fluorescence lifetime can often help to distinguish between static and dynamic fluorescence quenching processes. In the case of pure dynamic quenching process, the fluorescence lifetime ($\tau$) decreases continuously with gradual addition of quencher, which eventually gives a linear correlation of $\tau_0/\tau$ with quencher concentration. However, if the quenching process is purely static, then the fluorophore lifetime practically remains unaffected with the addition of quencher. To throw more light on this aspect for the present study, fluorescence lifetimes of both BA and DCBA have been measured in the presence and absence of variable amounts of all nitrophenol derivatives. Representative $\tau_0/\tau$ versus quencher concentration plots (presented in Figure S9) indicate that the lifetime values of BA and DCBA remain almost unaltered with the addition of nitrophenol derivatives, which essentially rules out the involvement of any collisional encounter between the excited fluorophore and the nitrophenol derivatives (i.e., dynamic quenching process) during the signaling event. Since there is some spectral overlap between the emission spectra of biaryl derivatives (BA and DCBA) and absorption spectra of nitrophenols (Figure S10), there could also be a possibility of energy transfer from BA and DCBA to nitrophenols for which quenching can be observed. However, since no change of lifetime values of BA and DCBA (here donor) could be observed with successive addition of quencher concentration, the possibility of energy transfer process in the present event is also ruled out.

The above discussion points out that the quenching mechanisms of BA and DCBA by DNP and NP (where no upward curvature could be observed) are purely static in nature. For BA derivative, the quenching constants for DNP and NP are estimated (from the $S-V$ plots) to be $3.75 \times 10^5$ and $1.27 \times 10^5$ M$^{-1}$, respectively. Similarly for the DCBA system, the quenching constants for DNP and NP are estimated to be $4.81 \times 10^5$ and $1.64 \times 10^4$ M$^{-1}$, respectively. Since no dynamic quenching process could be found for the quenching of BA and DCBA by PA, the upward curvature (Figure 15a,b) corresponding to this quenching event is analyzed further by invoking Perrin’s model of quenching sphere of action, which is represented by eq 2

$$\frac{F_0}{F} = (1 + K_{q}[Q]) e^{-V_{q}[Q]} \quad (2)$$

$$V_{q} = \frac{4}{3} \pi R_{q}^3 \times N_A$$

where $K_q$ is the quenching constant related to the linear portion of the $S-V$ plot, $V_q$ is the volume of quenching sphere in which quenching occurs without diffusion of the quencher molecule, $R_q$ is the radius of the quenching sphere, and $N_A$ is Avogadro’s constant. As can be seen from Figure 15, the data corresponding to $F_0/F$ and $[Q]$ can now be fitted nicely by employing eq 2. This observation clearly indicates that the quenching of BA and DCBA by Picric acid (PA) follows the quenching sphere of action model. The quenching constants ($K_q$) corresponding to quenching of BA and DCBA by PA are estimated to be $1.41 \times 10^5$ and $1.26 \times 10^5$ M$^{-1}$, respectively. The corresponding quenching sphere radii ($R_q$) for BA and DCBA are estimated to be 29.22 and 33.73 Å, respectively. Hence, we can say that in the case of PA, due to the formation of quenching sphere near the vicinity of fluorophore molecule, the highest (ca. 95%) efficiency for the quenching event is observed.

Note that the fluorescence quenching event of monoaryl systems (AN and CA) with nitrophenol derivatives exhibits no upward curvature in the $F_0/F$ versus $[Q]$ plot for the entire concentration range of the concerned quenchers (Figure S11). No change in the fluorescence lifetime values of AN and CA with the addition of quencher molecules has been observed. The linear $S-V$ plots in the case of PA and DNP for monoaryl system indicate that pure static quenching process is operating in these quenching events. The quenching constants for AN are estimated to be $5.69 \times 10^5$ and $5.48 \times 10^4$ M$^{-1}$ for PA and DNP, respectively, whereas quenching constants for CA are estimated to be $4.1 \times 10^5$ and $4.31 \times 10^4$ M$^{-1}$ for PA and DNP, respectively.

More interestingly, we note here that among the nitrophenols, the quenching efficiency follows the order PA > DNP > NP. Various factors such as hyperpolarizability, dipole moment, $\pi-\pi$ stacking, and weak interactions like intermolecular hydrogen bond are known to play an important role during fluorescence quenching of organic fluorophore by nitroaromatics. The observation of the aforementioned trend is attributed mainly to the $\pi-\pi$ interaction between $\pi$-conjugated molecules (used in this study) and electron-deficient nitrophenol molecules. It is highly likely that PA being the most electron-deficient among the three nitrophenols (PA, DNP, and NP), the quenching efficiency is observed to be the highest for PA with all of the studied fluorophore. We would like to stress that recently, Patra and co-workers have demonstrated that intermolecular interactions such as O–H···$\pi$ between $\pi$-conjugated molecule and nitrophenols can be responsible for nitroaromatics-induced fluorescence quenching of organic fluorophores. Considering this fact, in the present study, we can perhaps say that O–H···$\pi$ interaction can also play an important role for the formation of quenching sphere around BA and DCBA molecules, which eventually facilitates the quenching process. The higher quenching of fluorescence intensity of DCBA by PA than that of BA is an interesting observation. Note that phenolic hydrogen of PA is sufficiently acidic ($pK_a = -1.9$ in DMSO), and so it can additionally form intermolecular H-bond with the –CN group of DCBA. This additional (O–H···CN) interaction between nitrophenol and DCBA could be responsible for higher quenching of DCBA by PA. The observation of larger quenching for biaryl compared to monoaryl by nitroaromatic quenchers can be attributed to the presence of two anthracene rings in the case of biaryls. Fluorophore–quencher interactions are expected to be more for biaryl systems as two anthryl rings could facilitate more interactions (short contacts) with the studied quencher molecules.
3. CONCLUSIONS

In summary, two twisted biaryl molecules, namely, 9,9'-bianthryl (BA) and 10,10'-dicyano-9,9'-bianthryl (DCBA), have been synthesized and characterized by conventional spectroscopy methods. The photophysical properties of these systems are investigated in both solution and aggregated state and are compared to those of their respective monoaryl counterparts (AN and CA). A clear blue shift in the emission is observed for twisted biaryl systems upon aggregation. This effect is totally absent in the case of monoaryl systems. Additionally, the potential of these systems toward signaling of nitroaromatics explosive has also been explored. The signaling event is monitored by looking at the quenching of fluorescence intensities of different monoaryl and biaryl systems in the presence of various nitroaromatics independently. Several interesting aspects with regard to nitroaromatics signaling behavior by organic fluorophores have emerged during the signaling event. Among the nitroaromatics studied, the highest fluorescence quenching of the concerned fluorophore is observed by picric acid (PA). The study also reveals that quenching of fluorescence by PA is more for cyano-substituted BA derivative (DCBA) than for BA. Perrin’s model of quenching sphere action has been employed to explain the nitrophenol selective signaling behavior of biaryl systems. Interactions such as π-π, O-H···π, etc. between biaryl and nitrophenols is thought to be responsible for the observed fluorescence quenching of biaryl systems by nitrophenol derivatives. Due to highly acidic nature of nitrophenols, additional (O-H···CN) H-bonding interaction could be possible in DCBA, which, in turn, could be responsible for facilitating the quenching process. Interestingly, larger quenching for biaryl systems compared to monoaryl systems has been observed. Fluorophore-quencher interaction is expected to be more for biaryl derivatives due to the presence of two anthryl ring in biaryl systems.

4. EXPERIMENTAL SECTION

4.1. Materials. Anthracene, 9-anthracenecarbonitrile, anthrone, acetic acid, dimethylformamide (DMF), copper(I) cyanide, granulated zinc, and chloroform were purchased from Sigma-Aldrich and used without further purification. Concentrated hydrochloric acid was purchased from Nice Chemicals. Magnesium(II) sulfate and iron(III) chloride were obtained from TCI and used as received. Hexane and ethyl acetate used for column chromatography were received from Finar and used without further purification. Anhydrous solvents cyclohexane, toluene, dichloromethane, tetrahydrofuran, acetonitrile, and dimethyl sulfoxide used for photophysical studies were purchased from Sigma-Aldrich and used without further purification. CDCl3 was also procured from Sigma-Aldrich for recording NMR spectra. 4-Nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 4-nitrotoluene, 2,4-dinitrotoluene, and nitrobenzene were purchased from Alfa Aesar and used for sensing study.

4.2. Instrumentation. 1H NMR spectra were obtained on a Bruker BioSpin 400 MHz spectrometer at ambient temperature using tetramethylsilane as an internal standard. A Bruker micrOTOF-Q11 mass spectrometer was employed for the measurements of mass spectra. UV/vis and fluorescence spectra were recorded using a Cary 100 Bio UV/vis spectrophotometer and a Cary Eclipse fluorescence spectrophotometer, respectively. Time-resolved fluorescence measurements were carried out by using a time-correlated single-photon counting spectrometer (Edinburgh, OB920). A light-emitting diode laser, EPL 375 nm, was used to excite the molecule, and an MCP photomultiplier (Hamamatsu R3809U-50) was used as the detector (response time, 40 ps). The lamp profile was recorded by using a scatterer (dilute ludox solution in water) in place of the sample. Decay curves were analyzed by a nonlinear least-squares iteration procedure using the F900 decay analysis software. The quality of the fit was judged by the chi-squared (χ2) values and visual inspection of weighted deviations of residuals. In particular, a field emission scanning electron microscope from ZEISS was used to capture the images of organic aggregates. The aggregate sizes were determined through the dynamic light scattering (DLS) method using Malvern Zetasizer instrument.

4.3. Synthesis and Characterization. 4.3.1. Synthesis of 9,9'-Bianthryl (BA). 9,9'-Bianthryl was synthesized using a method reported in the literature. Typically 20 g of anthrone, 20 g of granulated zinc, and 100 cc of acetic acid were loaded in a two-neck RB flask and then heated under reflux for 8–9 h with dropwise addition of fuming HCl for the first 5 h only. Pale yellow crystals of 9,9'-bianthryl started to precipitate after a few hours. Then, the obtained compound was filtered and purified using column chromatography on silica using hexane and ethyl acetate (3:1) as the eluent. The yield of the obtained product was 75%. The compound was characterized using NMR and mass spectroscopy. 1H NMR: (400 MHz, CDCl3): δ 7.03 (d, 4H), 7.13 (d, 4H), 7.45 (d, 4H), 8.16 (d, 4H), 8.71 (s, 2H). Electrospray ionization mass spectrometry (ESI-MS): 354.41 (M+).

4.3.2. Synthesis of 10,10'-Dicyano-9,9'-bianthryl (DCBA). 10,10'-Dicyano-9,9'-bianthryl (DCBA) was synthesized using a method published by Mueller and Baumgarten. Typically 20 g of anthrone, 20 g of granulated zinc, and 100 cc of acetic acid were loaded in a two-neck RB flask and then heated under reflux for the first 5 h only. Pale yellow crystals of 10,10'-dibromo-9,9'-bianthryl and 1 g of CuCN in freshly distilled DMF and then refluxed for 3–4 h under an inert atmosphere. After that, the reaction mixture was cooled down and poured into a 1 M FeCl3 solution, which was then repeatedly extracted with CHCl3 and MgSO4 was used for drying. After that, the solution was concentrated and then the residue was chromatographed over silica gel with hexane and ethyl acetate (3:1) as eluent. The obtained product (yield 78%) was characterized using 1H NMR and mass spectroscopy. 1H NMR: (400 MHz, CDCl3): δ 8.64 (dd, 4H), 7.74 (m, 4H), 7.31 (m, 4H), 7.09 (d, 4H). ESI-MS: 404.43 (M+).

4.4. Fabrication of Organic Aggregates. The aggregates of AN, BA, CA, and DCBA were prepared using a well-known reprecipitation method. In short, 30 μL of a solution of each compound in DMSO (0.01 M) was rapidly injected through a syringe into 3 mL of Milli-Q water separately under vigorous stirring. The stirring was continued for about 20 min. The clear solution turns hazy, indicating the formation of aggregates. The formation of aggregates was confirmed by UV–vis absorption spectroscopy, FESEM images, and DLS method. To prepare the samples for FESEM study, freshly prepared diluted solutions of the aggregates were drop-cast on a clean silicon wafer surface and kept under vacuum for drying.
4.5. Determination of Fluorescence Quantum Yield.
Quantum yields (QYs) of AN, BA, CA, and DCBA in molecular and aggregated forms were measured following the standard procedure with quinine sulfate in 0.1 M H₂SO₄ (QY 0.54) as the reference compound. During QY measurement, the absorbances of both quinine sulfate dissolved in 0.1 M H₂SO₄ and the solutions of AN, BA, CA, and DCBA in DMSO were kept below 0.1 at the excitation wavelength of 350 nm. Optically matched solutions of reference and sample were used for measurement. Quantum yield was measured using the following equation (eq 3)

\[
QY_{\text{sam}} = QY_{\text{ref}} \times \frac{I_{\text{sam}}}{I_{\text{ref}}} \times \frac{A_{\text{ref}}}{A_{\text{sam}}} \times \frac{n^2_{\text{sam}}}{n^2_{\text{ref}}}
\]

where QY is the quantum yield, I is the fluorescence intensity, A is the absorbance, and n is the refractive index of the medium. The subscripts “sam” and “ref” represent sample studied and the reference used, respectively.

4.6. Characterization of Aggregates. The prepared aggregates were characterized using UV–vis spectroscopy, FESEM, and dynamic light scattering (DLS) techniques. During UV–vis spectroscopy, a red shift in the absorption spectra of the colloidal solution was observed. This observation is indicative of aggregate formation. Figure 16 shows the FESEM images of AN, BA, CA, and DCBA aggregates. The formation of aggregate and their size calculation were also investigated by dynamic light scattering (DLS) measurements (Figure 17).

The sizes calculated from DLS measurements are given in Table 3. It is observed that with increasing the size of the molecules, the hydrodynamic radius decreases, which is consistent with the literature reported data on some organic aggregated systems. The relatively larger size of smaller AN and CA molecules compared to larger molecules BA and DCBA is probably due to better packing of the AN and CA molecules in the aggregated state.

Table 3. DLS Data of AN, BA, CA, and DCBA in Aggregated form at Room Temperature

| system          | particle size (nm) |
|-----------------|--------------------|
| AN aggregate    | 250                |
| BA aggregate    | 220                |
| CA aggregate    | 230                |
| DCBA aggregate  | 180                |

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02232.

Normalized absorption spectra of AN and CA in some selected solvents (Figure S1); normalized absorption

Figure 16. FESEM images of (a) AN, (b) BA, (c) CA, and (d) DCBA aggregates at room temperature.

Figure 17. DLS plots of AN, CA, BA, and DCBA aggregates at room temperature.
spectra of AN and CA in their molecular form in DMSO and aggregated form in 99% water–DMSO mixture (Figure S2); normalized emission spectra of AN and CA in molecular and aggregated forms (Figure S3); normalized emission spectra of AN, CA, and BA in solid state at room temperature (Figure S4); time-resolved fluorescence intensity decay profiles of (a) AN and CA and (b) BA and DCBA in molecular form in DMSO and aggregated form (in DMSO–water mixture) (Figure S5); percentage fluorescence quenching efficiency of AN and CA with different nitroaromatics (Figure S6); fluorescence quenching spectra of BA and DCBA in the presence of quencher DNP and NP (Figure S7); fluorescence quenching spectra of AN and CA in the presence of quencher PA and DNP (Figure S8); relative fluorescence lifetimes plots ($\tau_0/\tau$) vs [Q] (say PA) for BA and DCBA (Figure S9); normalized absorption spectra of PA, DNP, and NP along with normalized fluorescence spectra of BA and DCBA showing spectral overlap (Figure S10); and S–V plots of $F_0/F$ vs [Q] for AN and CA fluorescence quenching by PA and DNP (Figure S11) (PDF)

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**Notes**
- The authors declare no competing financial interest.

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