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DISCUSSIONS

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# Advanced functional luminogens in the solid-state: general discussion

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**Andy Hor** opened a general discussion of the paper by Wenjing Tian: You have two types of crystal which are very interesting, and you related their crystal shapes to the nature of the intermolecular forces. Do you have any solid evidence that could support such a relationship, or this is purely a postulate based on observations of a body of systems? How many systems have you tried and are there any exceptions to the conclusions that you have drawn? We have recently reported similar observations and relationships but I wonder if yours are related to our systems. Also, you used trifluorotriiodobenzene in your aggregation study; what is the specific reason for choosing this in your study? In addition, what about repeating the experiments using triiodobenzene and trifluorobenzene as controls? What would you observe?

**Wenjing Tian** and **Bin Xu** both answered: We found that the crystals possess a 2D-like morphology such as block-like or slice-like when there are some strong pi-pi interactions between adjacent molecules, whereas the crystals tend to form a 1D-like morphology such as needle-like when there are some weak H-bond interactions between adjacent molecules. The reason for using trifluorotriiodobenzene in our case was to try to introduce H-bond interactions such as C-H…F and C-I…N interactions into the aggregation. These H-bonds provide more opportunity to form various aggregate structures, which is beneficial to understand the relationship between the molecular structure, stacking modes and photophysical properties.

Up to now, we have not used triiodobenzene or trifluorobenzene to grow the co-crystals. This is a very good suggestion, and we will certainly investigate that.

**Ben Zhong Tang** commented: This FIB molecule is electron deficient. BP4VA is different from DSA in your previous work as it is AEE, while that was AIE. Can you explain the difference? BP4VA is a TICT molecule, so have you checked the solvent polarity effect?

**Wenjing Tian** and **Bin Xu** responded: This is a very good question. Actually, we have developed several DSA derivatives with different electron donating or accepting groups on the periphery. BP4VA is one example and has two electron withdrawing pyridines substituted on the benzene of DSA. Based on spectroscopic studies, we found that modification of the electron withdrawing group makes the electron density distribution of the molecular orbitals (MOs) tend to be more delocalized, which is contrary to what is necessary for AIE. Normally, the electron transition of the DSA derivative under photoexcitation mainly comes from the central divinylanthracene (DVA) part, which is the intrinsic origin of the AIE feature. If we introduce an electron acceptor into the DVA backbone, the distribution of the MOs will more delocalized and the AIE effect will be weaker. This is the reason that BP4VA shows an AEE, whereas the AIE effect will be increased when an electron donor is introduced. Indeed, BP4VA is a TICT molecule and shows a typical solvatochromic effect.

**Govindarajan Krishnamoorthy** remarked: This is nice work. What is the dipole moment of the system? What happens when you change the side groups and solvent polarity? There may be some ICT, not TICT, in your present system.

**Bin Liu** also commented: I'd like to follow on from the TICT and AIE question. If you put a compound in DMF or DMSO there is no fluorescence so you can define it as AIE. I have a strong objection to that. If you start with hexane or THF, it is not an AIE molecule any more. How can a molecule be AIE or not depending on the solvent?

**Ben Zhong Tang** answered: When a luminogen has a TICT feature, the situation becomes complex. It could be AIE, AEE or even ACQ, depending on the interplay of the constructive and destructive forces that affect the emission behavior of the luminogen. While this makes the issue complicated, it, on the other hand, offers the opportunity to develop new stimuli-responsive luminogen systems, if the TICT process can be smartly utilized.

**Ben Zhong Tang** then asked: If you use triiodobenzene or trifluorobenzene, what would happen? Surely triiodo is a very good quencher? Have you measured the lifetime?

**Bin Xu** answered: Thank you very much for your kind suggestion. We believe we can get some different luminescent properties and stacking modes of the co-crystal, since various supramolecular interactions with triiodobenzene or trifluorobenzene are introduced. With regard to fluorescence quenching of the triiodo co-crystal existing, the heavy atom effect should be taken into account. However, in due course we will reach a conclusion regarding that, and we will keep trying to investigate the nature of this behavior. We have measured the lifetime of these two crystals; the lifetime of the two co-crystals is short compared with the pure BP4VA crystals.

**Bin Liu** remarked: I'm always puzzled about red-emissive AIE molecules which have strong ICT characteristics. When we use these in cells / tumours, the environment is hugely changed. Surely TICT contributes significantly, and many of us draw the conclusion that this is an AIE event and that this is due to the change in polarity of the solvent.

**Ben Zhong Tang** responded: In this particular case, it is an AIE event by definition. In an aqueous medium, a TICT luminogen is often non-emissive. When its molecules are aggregated inside tumor cells, the RIM mechanism comes into play, thus turning on the light emission. TICT is a "good" effect in terms of helping the red-shift of the emission color of a luminogen.

**Eric Rivard** opened a general discussion of the paper by Fuyuki Ito: Regarding your multi-component analysis, what is your sensitivity – 10%, 1% of a component? This could be a general tool for everyone in the community if it is easy to implement.

**Fuyuki Ito** responded: There is no general answer to your question as the amount of variance due to each component is data dependent, but any significant signal variation can be explained, provided that it is higher than the S/N ratio.

**Bin Liu** commented: I have a strong interest in this paper. We discussed this at our group meeting. It's great. There are too many things we don't understand why they happen, and this paper helps us to find a way to understand the process of how molecules self-assemble. I think it's great work.

**Fuyuki Ito** responded: Thank you for your comments, which we are glad to have. We are going to use the present method for various molecular systems.

**Bin Liu** then asked: When you fit the curves for different data points and different species, there are multiple ways to fit the centre of the curve, so how did you decide which way to choose to fit the curves for your data?

**Fuyuki Ito** answered: The Multivariate Curve Resolution – Alternating Least-Squares (MCR-ALS) method contains a group of techniques which is intended to be used to recover the pure spectra of chemical constituents or species of an unresolved mixture when no prior information is available about the nature and composition of these mixtures. The detail of the MCR-ALS method is described in the following web page: https://mcrals.wordpress.com/

**Yoshiki Chujo** asked: Can you comment on the effect of the temperature dependence for the amorphous state?

**Fuyuki Ito** responded: We have no information about the temperature dependence of the amorphous state. The amorphous state is prepared by rapid quenching of the molten state, the state of which is not stable at ambient temperature. Interestingly, the mutual state of the crystal formation process we can detect seems to be the amorphous state even at ambient temperature. We need to clarify the thermal stability of the amorphous state in the non-equilibrium state during the crystal formation process.

**Bingshi Li** remarked: When monitoring the molecules, have you changed the concentration or volume of the solution used for the reaction? It seems like these factors are crucial for the self-assembly of your system. In our group we have carried out similar experiments and changed the volumes, and if the volume is too small, it is difficult to monitor the morphology of the aggregates. In addition, how can you ensure that the aggregates you observe are crystalline instead of just normal aggregates?

**Fuyuki Ito** responded: According to your comments, the concentration and volume of the solution were changed as a function of time for the evaporative crystallization system. The solvent evaporation causes the driving force for the assembly. A number of molecules in the system remained on the substrate.

We confirmed the aggregates formed using a polarized optical microscope, whether they were in the crystalline state or not.

**Andrea Pucci** asked: You showed us the spectra as a function of concentration, and I was wondering about the behaviour, as we see a blue-shift in emission, and I'd like your clarification.

**Fuyuki Ito** answered: The fluorescence spectra were red-shifted with increasing concentration. The fluorescence excitation spectra, on the other hand, showed a blue-shift with increasing concentration. As indicated in the main text of our paper, and as shown in Fig. 5, the fluorescence excitation spectra indicated a contribution from the H-aggregates. This contribution suggests several mechanisms: (i) energy transfer from the H-dimer to the J-dimer acting as a trap site; (ii) a low exciton trapping probability in the uniform crystal structure induced by tight stacking of cyanostilbene motifs; and (iii) weak coupling caused by molecular distortion such as oblique aggregation leading to the transition being partially allowed from the lower energy site. In any case, the emission from the H-aggregates is still under investigation.

**Yuguang Ma** said: This is a very interesting study. It is very important to understand the crystal processes. Are you trying to control the nucleation and get a different crystal and control the earlier state?

**Fuyuki Ito** responded: Thank you for your message about our study. I guess it is hard to control the nucleation process including the polymorph formation in the present state. However, it is a very interesting and important issue.

**Govindarajan Krishnamoorthy** commented: You have performed ground state calculations, but excited state calculations might provide a clear answer to support your mechanism. However, I agree with you that excited state optimization may be computationally expensive.

**Gang He** opened a general discussion of the paper by Anjun Qin: Your solution shows bright blue emission when the water fraction is 70%; do you know the conformation and molecular packing in this state? If you believe the solvent polarity causes this effect, maybe you can do some calculations to study this? As you have the quantum yield in different solvents, can you give some further information here?

**Anjun Qin** replied: Thank you for your question. We also want to know the molecular conformation and packing in the THF/water mixtures with different water fractions, but it is quite difficult. The emission in the THF/water mixture with a water fraction of 70% is almost quenched according to our experiments. This phenomenon is ascribed to the TICT process due to the increase in the solvent polarity upon addition of highly polar water into THF. The conclusion was confirmed from the solvatochromism effect of TPB-AC in organic solvents with different polarity, as shown in Fig. 2 of the paper.

For TPB-AC, we have not measured its quantum yield in different polarity solvents. However, the quantum yields of its nanoparticles, film and powder were measured. All show high values.

**Guichao Kuang** remarked: Why do you see strong blue emission, and why is this colour so interesting?

**Anjun Qin** responded: Thank you for your question. According to our previous work,[1] TPB emits at 380 nm, which could not be observed by our eyes. To red-shift the emission of TPB, one strategy is to conjugate with donors and acceptors. In this work, we introduced an electron-accepting cyano group and an electron-donating diphenylamine group on the TPB core. Thanks to the intramolecular charge-transfer, blue emission of TPB-AC was successfully realized.

1. L. Z. Li, M. Chen, H. K. Zhang, H. Nie, J. Z. Sun, A. J. Qin and B. Z. Tang, *Chem. Commun.*, 2015, **51**, 4830–4833.

**Eric Rivard** asked: Do you have an idea of the stability of your device over time? Looking at the nature of the HOMO and LUMO states involved during excitation, you may have a chance for TADF (thermally activated delayed fluorescence). Accordingly, do you see two lifetime components (one long, one short) during luminescence?

**Anjun Qin** responded: Thank you for your questions. Theoretically, stable OLEDs can be obtained with our molecule as the emitting layer. We can enhance the device stability over time through further optimization of the device configuration. Looking at the HOMO and LUMO of our molecule, there is a slight overlap between them, and thus it does not show TADF. This conclusion was confirmed from its relatively short lifetime (3.19 and 3.14 ns in THF solution and film states, respectively). Only one lifetime component was observed during measurement.

**Yuguang Ma** remarked: What is the effect of solvent polarity on TICT?

**Anjun Qin** responded: In general, a TICT process happens in a fluorophore with a donor–pi–acceptor structure. Thus, intramolecular charge transfer is often observed for such a system in a polar solvent. For an AIEgen with a donor–pi–acceptor structure, besides the solvent polarity, its solvating ability also affects its emission especially in solvent mixtures with a high fraction of poor solvent due to the restriction of intramolecular rotation.

**Youichi Tsuchiya** asked: In Fig. 1 of your paper, the spectra look like giving sky blue emission, but in the device it is deep blue EL emission. So why is there this difference? Secondly, have you tried using these as dopant materials in a host matrix?

**Anjun Qin** answered: Thank you for your questions. From the structure of TPB-AC, we can know it contains a donor and acceptor, thus, this molecule shows a solvatochromism effect. THF is also a kind of polar solvent although its polarity is not as high as DMF. When TPB-AC is dissolved in THF, the intramolecular charge transfer (ICT) process can occur. Meanwhile, in the film state, there is no polarity effect on the molecule, and the ICT process is suppressed to some degree. Thus, the EL of TPB-AC is blue-shifted compared with its PL in THF. Because TPB-AC is highly emissive in the film state, we have not tried to dope TPB-AC in a host matrix to fabricate OLEDs.

**Zhen Li** commented: In your molecular structure, there are some triphenylamine moieties, which are hole transporting groups. Have you tried to remove the NPB to see the effect?

**Anjun Qin** replied: Thank you for your good question. Yes, we also want to fabricate devices without the hole transporting layer but have so far failed.

**Shuizhu Wu** said: When I look at the structure of your compound, I wonder whether a similar compound without a cyano group may serve the same purpose. Have you ever synthesized the compound without a cyano group as a control? It might also be a very good blue emitter, and its emission won't be dependent on the solvent polarity.

**Anjun Qin** answered: Thank you for your comments. We are sorry that we have not synthesized the compound without the cyano group. TPB-AC emits in the blue region. If no electron-donating group is connected, the compound probably will emit in purple–blue region instead of the blue region due to the lack of an ICT process. I also think that no solvatochromism will be observed if such a compound is synthesized. Thank you again.

**Kun Wang** commented: Thank you for your presentation. In Fig. 1b of your paper, there is a sharp increase from 70–80% in water fraction, but from 80–90% there is a small decrease in intensity. How can you explain this small decrease?

**Anjun Qin** replied: This is a very good question. We have not checked this yet for our system.

However, this phenomenon has often been observed in other AIE systems. One possibility is that micro-crystals are formed in the THF/water mixture with water fraction of 80%, which could lead to the enhancement of the emission. Meanwhile, in the THF/water mixture with water fractions more than 80%, amorphous aggregates are formed, which are not as emissive as the micro-crystals.

**Yoshiki Chujo** opened a general discussion of Wenjing Tian's, Fuyuki Ito's and Anjun Qin's papers: The purity is very important as this affects the properties we see. Could you comment on the impurities in your compounds and the effect on the properties you observe.

**Anjun Qin** responded: I agree with Professor Chujo's comment that the purity is very important because it will affect the property of a compound. Thus, we measured the properties of TPB-AC after purification with column chromatography and characterized it using proton and carbon NMR as well as high resolution mass spectra.

**Wenjing Tian** replied: Thank you very much for your kind comments. Indeed, the purity plays a very important role regarding the properties of organic materials. In our case, we used chromatography and vacuum sublimation methods to purify the compounds and the purity of our samples should be greater than 99%. On the other hand, crystallization itself is a purification process, although there are often small impurities in organic single crystals. Regarding the effect of impurities on the properties of organic luminescent crystals, we cannot observe any influence on the luminescence properties such as emission color, wavelength and efficiency in our case. Such impurities may affect the optoelectronic properties of organic materials in other states, such as powders or films, whose purities are often lower than single crystals.

**Fuyuki Ito** also responded: We checked the purity of the fluorescence molecules using elemental microanalysis in addition to TLC, NMR, and fluorescence measurements before the measurements. These are important for fluorescence measurements especially in the solid state.

**Eric Rivard** commented: In our lab we commonly do elemental analysis to determine purity prior to making luminescence measurements, as NMR is generally not an ideal method to verify sample purity.

**Bin Liu** opened a general discussion of the paper by Eric Rivard: Nice work. I'd like your clarification on one point. You say that your molecule shows room temperature phosphorescence, but then you said that it is not stable, or is not stable to oxygen? Did you ever study the phosphorescence under vacuum? Where does the energy go? Can you prevent this? You should make your crystals as small as possible to maximize the surface area. This will really increase the ratio.

**Eric Rivard** answered: All of the compounds I showed are stable to air in the solid state. As for the initial compound I presented, **B-Te-6-B** (see Scheme 1 in the paper), it is stable in both water and oxygen and can even be purified using column chromatography. We have made PL measurements of this species under vacuum and see similar emission profiles as under 4 atm of $O_2$.[1] We also see a pronounced effect related to the quantum yield of phosphorescence depending if we drop or spin-cast films of this compound from THF. Spin-coating leads to a more inhomogeneous and less crystalline film, and accordingly we see a substantial drop in quantum yield as a result (from *ca.* 15% to about 1%).[2] At this stage we think that in the solid state, the amount of phosphorescence quenching by $O_2$ is limited due to suppression of oxygen diffusion through the crystalline films of **B-Te-6-B**.

1. G. He, B. D. Wiltshire, P. Choi, A. Savin, S. Sun, A. Mohammadpour, M. J. Ferguson, R. McDonald, S. Farsinezhad, A. Brown, K. Shankar and E. Rivard, *Chem. Commun.*, 2015, **51**, 5444–5447.
2. A. Mohammadpour, B. D. Wiltshire, S. Farsinezhad, Y. Zhang, A. M. Askar, R. Kisslinger, W. T. Delgado, G. He, P. Kar, E. Rivard and K. Shankar, *Org. Electron.*, 2016, **39**, 153–162.

**Andrea Pucci** remarked: To follow on from Prof. Liu's question, is that why you cast under nitrogen?

**Eric Rivard** responded: In the case of the yellow emissive species **$ImMe_2{}^iPr_2 \cdot$B-Te-6-B**, we cast the films under nitrogen as this species is moisture sensitive in solution. The main reason being that in solution one can remove the bound carbene unit by protonation. To avoid this possible side reaction, we conducted all sample preparations and optical measurements under nitrogen.

**Youichi Tsuchiya** asked: Did you check for NIR emission of your 'non-emissive' compound?

**Eric Rivard** answered: We have not at this stage due to equipment limitations, however, recently our university has acquired a fluorometer equipped with an IR detector. Although we do not expect emission from borylated tellurophenes with Lewis bases coordinated at boron (which effectively shuts down the excitation leading to phosphorescence) we really need to check this spectral region to be sure. Another reason for scanning the IR region is to look for emission from singlet oxygen. It is well known that many species exhibit minimal or no phosphorescence as a result of quenching of the excited triplet states by triplet oxygen; the by-product of this process is highly emissive singlet oxygen which emits at 1268 nm.

**Anjun Qin** commented: Thanks for your interesting talk. There are four B–C single bonds in one molecule. We all know such a bond is unstable, especially under basic conditions. Have you checked the chemical stability of these compounds under basic conditions?

**Eric Rivard** responded: In a recent paper[1] we showed that tellurophenes with pinacolboronate (BPin) groups are indeed sensitive to base (but not acid). The main issue is the low electronegativity of tellurium which makes the adjacent carbon atoms quite electron rich. Thus when a base coordinates to the BPin group, effective protodeboronation occurs in the presence of water, whereby direct protonation of a carbon center and loss of a BPin group *via* B–C bond cleavage occurs. This is the main reason why using our BPin-capped tellurophenes in Suzuki-Miyaura cross-coupling is so challenging.

1. W. T. Delgado, F. Shahin, M. J. Ferguson, R. McDonald, G. He and E. Rivard, *Organometallics*, 2016, **35**, 2140–2148.

**Rongrong Hu** asked: I am interested in the role the boronic ester group plays in your system. When they are substituted on the 3,4-positions, it seems they do not contribute much to the conjugation. Why is the boronic ester group essential for phosphorescence at the 2,5-positions?

**Eric Rivard** responded: At this stage we do not know the full reason why BPin groups at the 2,5-positions are required for solid state phosphorescence. Our calculations do show that the p-type orbital on boron is involved in the excitation and emission processes, but we would like to build a greater library of possibly phosphorescent tellurophenes in order to better understand the structural requirements for emission

**Jing Zhi Sun** asked: I noticed that the singlet and triplet energy levels have been drawn quite near. This is very important in tuning emission in organic light emitting materials. How do you achieve the alternation of the HOMO–LUMO pattern in your molecules?

**Eric Rivard** responded: You are correct in saying that obtaining close singlet–triplet (S1–T1) states generally requires electron density in the HOMO to be in different regions than the LUMO. In our case, the closest energies involve the S1 and the higher triplet state (T3), thus we do not need as strict a requirement to achieve mixing between the singlet and triplet states. This also means that the relative energies of the S1 and T3 are sensitive to the placement/nature of the substituents about the Te ring, and thus could explain why many of our derivatized tellurophenes are not phosphorescent.

**Govindarajan Krishnamoorthy** opened a discussion of the paper by Osamu Tsutsumi: How does the alkyl chain length affect the luminescence? Do you have any excimer formation?

**Osamu Tsutsumi** answered: In our molecular systems, the luminescence behavior is affected by the structure of the molecular aggregates. The length of the alkyl chain does not affect the luminescence directly. However, the alkyl chain affects the aggregated structures, therefore, our molecules change the luminescence behavior *via* the length of the alkyl chains. The emission of our molecules comes from the molecular aggregates, *i.e.* dimer, trimer, or oligomer. Those aggregates formed in the ground state in the crystal; namely, the aggregate acts as one luminogen. So in the crystal and liquid crystal, we have this kind of emission from the aggregates, which is similar to the excimer emission. In solution ($<10^{-3}$ mol $L^{-1}$), we did not observe excimer formation.

**Andy Hor** commented: Gold compounds undergo ‘aggregation' but this comes broadly in two forms: covalent bonding, which is what many people call “aurophilic bonding” (this is well-established), or aggregation as you define it with weak intermolecular interactions. Your description of aggregation appears to be on the latter. How did you rule out the possibility of aggregation through covalent bonding, especially Au–Au bonding as this is very common in the literature? Even in your description of a single Au(I) molecule undergoing aggregation over a range of temperatures, you seem to assume that there is no Au–Au interaction which could lead to oligomerisation and formation of polynuclear gold complexes. Is that true? What is so special in your system that precludes the formation of Au–Au bonding? What exactly is the role of Au–Au interactions in this type of aggregation that you describe? I am trying to relate your systems to the many Au(I) systems that undergo various forms of aggregation in the literature.

**Osamu Tsutsumi** answered: According to Schmidbaur *et al.* (for example, see ref. 1), the bond length of the Au–Au covalent bond is 2.5 Å; however, in the case of non-covalent Au–Au interactions, which are known as aurophilic interactions, Au–Au distances are typically 2.8–3.3 Å. Generally, when the interatomic distance between two Au atoms is well below the sum of the van der Waals radii (~3.6 Å), we can consider that a non-covalent aurophilic interaction exists. In this paper, we consider that the molecules are aggregated into crystals and liquid crystals (LC) by non-covalent aurophilic interactions. We estimated the distance between Au atoms in the crystal from the single-crystal X-ray structural analysis, and revealed that the shortest Au–Au distances were 3.42 Å for complex **B3**, and 3.32 Å for complexes **B5** and **B7** (see Fig. 2 in our paper). These results clearly indicate that the interaction between the Au atoms is non-covalent bonding, *i.e.* an aurophilic interaction. On heating the materials above their melting points, they showed a LC phase. In this phase, they exhibited almost the same shape in their luminescence spectra (Fig. 6). Thus, we also consider that the same non-covalent interaction exists between Au atoms in the LC phase.

1. H. Schmidbaur, S. Cronje, B. Djordjevic and O. Schuster, *Chem. Phys.*, 2005, **311**, 151–161.

**Ben Zhong Tang** said: Following on from Prof. Hor's comments, it would be useful to obtain crystal structures or measure XRD diagrams at different temperatures to investigate the Au–Au interaction. Another research group led by Prof. Shenghua Liu at Central China Normal University in Wuhan have studied similar systems and they reported many crystal structures which do not involve Au–Au interactions.[1–3] Another group led by Professor Jianping Xie at the National University of Singapore has also published papers on the AIE activity of gold complexes.[4,5]

1. J. Liang, Z. Chen, J. Yin, G.-A. Yu and S. H. Liu, *Chem. Commun.*, 2013, **49**, 3567–3569.
2. Z. Chen, J. Zhang, M. Song, J. Yin, G.-A. Yu and S. H. Liu, *Chem. Commun.*, 2015, **51**, 326–329.
3. J. Liang, Z. Chen, L. Xu, J. Wang, J. Yin, G.-A. Yu, Z.-N. Chen and S. H. Liu, *J. Mater. Chem. C*, 2014, **2**, 2243–2250.
4. Z. Luo, X. Yuan, Y. Yu, Q. Zhang, D. T. Leong, J. Y. Lee and J. Xie, *J. Am. Chem. Soc.*, 2012, **134**, 16662–16670.
5. N. Goswami, Q. Yao, Z. Luo, J. Li, T. Chen and J. Xie, *J. Phys. Chem. Lett.*, 2016, **7**, 962–975.

**Youichi Tsuchiya** commented: We see the emission depends on the alkyl chain length, but is there any evidence that the emission depends on the Au–Au distance? In compound **B9** the quantum yield decreased suddenly – why?

**Osamu Tsutsumi** responded: In our molecular systems, the luminescence behavior is affected by the structure of the molecular aggregates, but is not affected by the alkyl chain length directly. In the present system, we consider that not only the Au–Au distance but also the formation of a 2-dimensional structure is important for the luminescence behavior; formation of a 2D structure enhanced the luminescence. Thus, the emission behavior does not show a simple dependence on the Au–Au distance. In the case of compound **B9**, we do not have a clear idea of why it showed lower quantum yield than the others. Due to the long alkyl chain, the degree of crystallinity might be decreased in this compound, and this is one possibility for the low quantum yield in compound **B9**.

**Zujin Zhao** asked: Do you have any evidence to confirm the lifetime of the emission? Which kind of structure can generate phosphorescence?

**Osamu Tsutsumi** responded: We measured the lifetime of the emission; it is in μs order, so we can conclude that the emission is phosphorescence. We also discussed the relationship between the crystal structure and emission efficiency. We conclude that the phosphorescence is generated by the aggregated structure (dimers, or more) and that the 2-dimensional layer structure in the crystals enhanced the phosphorescence.

**Fuyuki Ito** commented: It is interesting to accelerate the intersystem crossing process by aggregation induced enhancement. What is the reason for controlling the intersystem crossing by aggregation?

**Osamu Tsutsumi** responded: We do not understand the emission mechanism exactly. In the case of our gold complexes, the direct S0–T1 transition (LMMCT transition) was significantly observed; in this case, the transition from the π orbital to the metal d orbital occurred. This electronic transition should accompany a large change in the angular momentum of the orbital, and we consider this to be one reason why the materials showed efficient intersystem crossing. However, investigation about the mechanism is still ongoing.

**Deqing Zhang** said: The crystal structure is very ordered. Did you study its semiconductivity and mobility? Did you measure the semiconductivity by making a field effect transistor?

**Osamu Tsutsumi** replied: We have measured the semiconductivity of our materials using electrochemical impedance spectroscopy, and the materials reported in this paper showed a conductivity of $10^{-8}$ S $cm^{-1}$. The observed conductivity is lower than expected, because we used a pellet of micro-crystals as a sample for this measurement. We believe that when we measure it with a single crystal or uniaxially-aligned liquid crystals, we will get a much higher conductivity.

**Gang He** asked: Is the excitation profile the same or different for the fluorescence and phosphorescence? If they are different, are the emission properties different in the excited state? Maybe this means that you are forming it in the ground state rather than the excited state.

**Osamu Tsutsumi** answered: The excitation profile of the fluorescence band is different from that of the phosphorescence band, because in our molecular system a significant amount of the triplet state was generated by the direct excitation from the ground state.

**Jing Zhi Sun** said: The mechanism of AIE is generally RIR/RIV. In your system the emission is induced by the formation of a new luminogen. In other words, this observation can be considered as aggregation-induced formation of the luminogen. This is quite different from "classical" AIE systems. In those "classical" systems, the luminogens are always there in a chemical sense, no matter if they are in free or in aggregation states. However, they are non- or weakly emissive in dilute solution, while being highly emissive in the aggregation state. In the gold complexes, the luminogens are not there before aggregation; chemical bond formation is the precondition. I think this is something new.

**Ben Zhong Tang** addressed Jing Zhi Sun: If you have the formation of Au clusters, then following on from Prof. Sun's comments, once cast it can serve as a chromophore to emit light. But Prof. Sun's case is a bit different as the molecule is conjugated, so it is probably a combination of aggregation and cluster formation.

**Jing Zhi Sun** replied: From the crystallographic picture, I did not see Au clusters, but saw two well-arranged molecules conjugating with a Au–Au bond. I think that this AIE system is a new style: aggregation-induced formation of a luminogen, by which I mean that there is no luminogen before the aggregate forms. In conventional AIE systems, there are luminogens before and after aggregate formation. However, they are weakly emissive in the free motion state and strongly emissive in aggregates.

**Yuan Gu** asked: What is the pH of the buffer you use to analyze the assay? At this pH, what is the charge of BSA in this solution? In addition, does the positively charged probe prefer DNA or protein binding?

**Jing Zhi Sun** replied: In most cases, we used routine phosphate buffer and adjusted the pH to a final value of 7.4 before analyzing. At this pH value, normally, BSA is neutrally charged. The positively charged probe **M3** prefers DNA to protein kinetically; we have published a paper on this.[1] Due to the immediately electrostatic interaction between the positively charged probe molecules and negatively charged DNA, I think that the probe will prefer to be bound by DNA. In another study,[2] we found that **M3** can intercalate between the base-pairs. This is strong evidence and implies that the binding between **M3** and DNA is not only kinetically preferred, but also thermodynamically stable. Rationally, we deduce that **M3** prefers DNA to protein.

1. J. Jin, X. Chen, Y. Liu, A. Qin, J. Z. Sun and B. Z. Tang, *Acta Polym. Sin.*, 2011, **9**, 1079–1085.
2. Y. Chen, K. Ma, T. Hu, B. Jiang, B. Xu, W. Tian, J. Z. Sun and W. Zhang, *Nanoscale*, 2015, **7**, 8939–8945.

**Xuewen He** asked: You have fluorescence when **M2** binds to BSA, but no fluorescence when binding to DNA; how long was the DNA chain length? If the DNA chain is not very long, then BSA and DNA are not comparable here because the molecular weight of BSA is about 65 kDa. Also, BSA is inclined to form a dimer at pH 7.4. In your study, do you have a control? Finally, the dielectric charge on the surface or inside the BSA is very different at different pH values. So in your buffer solution, the charge on the BSA should be negative. Have you tried using other proteins that have different isoelectric points?

**Jing Zhi Sun** responded: We did not measure the fluorescence response of **M2** to DNA in the presence of protein BSA. I just said that **M2** (in fact it is **M3**) may have a weaker binding ability to DNA than to BSA. I just want to know the binding behavior of BSA. Other proteins may disclose some useful information, but that would be indirect.

**Govindarajan Krishnamoorthy** remarked: How do you know that the molecules are in an aggregated form inside BSA? Do you have any proof? It may be in the monomer form and upon host–guest complexation, depending on the binding site, not only the restriction of internal motion of the guest can cause enhancement in fluorescence, but also the hydrophobicity of the environment.[1]

1. N. Dash, A. Mishra and G. Krishnamoorthy, *J. Pharm. Biomed. Anal.*, 2013, **77**, 55–62.

**Ben Zhong Tang** asked: To rephrase Dr Krishnamoorthy's question, is it the monomer or the aggregate emitting? I guess we see emission from both species. Why? The emitting part is hydrophobic, so it is likely that many molecules will enter the same hydrophobic pocket, but it is very difficult to differentiate and tricky to answer.

**Jing Zhi Sun** answered: I did not say that the probe molecules form an aggregate inside BSA. AIE, or aggregation-induced emission, is only a phenomenological description. The underlying mechanisms are restricted intramolecular rotations and vibrations. Even when a single probe molecule binds to a hydrophobic pocket of a protein, these restrictions can be triggered and emission will be turned on. This is the same as you mentioned. If you look at the figures in our paper, you can see that we actually put one probe molecule rather than a cluster into the binding domain of the BSA.

**Youichi Tsuchiya** asked: Have you measured the Job's plot between BSA and the compound? A Job's plot should make the binding ratio clear.

**Jing Zhi Sun** responded: Thanks for the suggestion. However, we have not carried out this very careful and systematic measurement, because the essence of this work is not to detect BSA, but to try to know something about the unfolding and refolding processes of BSA. Fluorescence is a technique characterized by its high sensitivity, thus we can use trace amount of the probe molecule for the investigation. We do not need to check the effect of the probe concentration within a large scope for the response of BSA. Alternatively, we checked the effect of protein concentration on the fluorescence response of the BSA+probe systems.

**Ben Zhong Tang** opened a general discussion of the paper by Pengfei Duan: Very nice work. Have you checked the upconversion CPL?

**Pengfei Duan** answered: Not yet, but we are now doing that.

**He Tian** asked: As displayed in your fluorescence spectrum, is the emission colour near white?

**Pengfei Duan** replied: Not really. The acceptor compound showed solvatochromism in various solvents. In polar solvents, like DMF, the emission peak showed a red-shift and broadening. This covers a wide range from 450 to 650 nm and is close to white emission. But the observed color is yellow–green.

**Andy Hor** commented: You mentioned the use of Pt and Pd complexes with nitrogen macrocycles as sensitizers; what is so special about these two complexes over a range of other alternative complexes? Can you comment on their specific role and influence on the nature and degree of upconversion?

**Pengfei Duan** answered: The Pt and Pd porphyrins have been widely used as TTA-UC sensitizers (donors) due to their high yield and long lifetime of the triplet exciton. In particular, studies regarding TTA-based upconverted emission from green (532 nm) to blue have mostly concentrated on Pt and Pd porphyrins because the Q-band of the porphyrins for absorption is located around 532 nm. Some other metal complexes have also been reported as donors for TTA-UC such as Ir complexes. However, severe reabsorption (the donor could reabsorb the upconverted emission) might prevent efficient TTA upconversion emission. In terms of the spectral results, if the absorption peak of the Pd porphyrin could avoid overlap with the emission of the acceptor, this would give the best combination of donor and acceptor for TTA-UC.

**Youichi Tsuchiya** said: Have you tried to construct TTA-UC using the **D-1** and **L-2** molecule? These two molecule have opposite chirality. If you use **D-1** and **L-2**, do you see the same upconversion property as the **L-1** and **L-2** system ?

**Pengfei Duan** responded: The **D-1**/**L-2** combination exhibited a similar assembly behavior (Fig. S4 shows the morphology of the co-gel made from **D-1**/**L-2**). We did not report the upconversion emission results in this work. In fact, the UC emission was similar to the combination of **L-1**/**L-2**. Because the mixing ratio of acceptor/donor is very large value (500/1), a small amount of **L-2** will not tremendously change the emission behavior of **D-1**.

**Bingshi Li** asked: For the structures of **L-1**/**D-1**, the alkyl group has a long chain; is there a specific purpose for this length? Are they a spacer to separate the molecules from each other? How can you define whether it is well ordered?

**Pengfei Duan** answered: The length of the alkyl chain in **L-1**/**D-1** is C12. This lipid moiety has been widely applied in other works due to its excellent self-assembly behavior. The alkyl chain was introduced to improve the assembly behavior, not just to separate the chromophores. This moiety also has been reported as a chiral lipid which can form well-ordered chiral structures. We can confirm the molecular packing by checking the morphology and X-ray diffraction results. In this work, we observe uniform chiral structures using scanning electronic microscopy. We believe the gelators showed well-ordered chiral assembly during the gel formation. If you are asking about Fig 4a in our paper, that is the UC spectrum. The broad peak is the UC emission peak. The narrow one is the remaining part of the 532 nm green laser after filtering with a 532 nm notch filter.

**Dario Pasini** commented: You use natural glutamic acid to introduce chirality in your π-conjugated systems, which assemble *via* intermolecular hydrogen bonds between the amide functionalities into gels. However, glutamate is a multivalent system, with each unit possessing up to three amide units being potentially involved in the assembly process. Have you thought about using simpler chiral amides to end-cap your conjugated system, which could yield more regular structures?

Additionally, your CD spectrum shows induced CD activity into the π-conjugated chromophoric band. Can you comment on this?

**Pengfei Duan** responded: Thank you for your suggestion. In this work, we used glutamate lipid as the assembly moiety due to the strong intermolecular interactions of the three amide units and the long alkyl chains. We expected to obtain good assembled structures in this design. Because we didn't try using other simple chiral amides, it is difficult to comment on the emission properties. For the CD spectra, the observed strong Cotton effect can be assigned to the chromophoric band. The chirality of the glutamate could be transferred to the chromophore during the gel formation and expressed as the induced supramolecular chirality. This general phenomenon has been widely demonstrated in π-conjugated gel systems.[1] One generally accepted mechanism of induced supramolecular chirality in chiral gel systems is that, in the gelation process, chirality can be transferred from gelator molecules to the self-assembled aggregates. In the presence of a chromophore, there will be an exciton and alignment of chiral molecules to induce a signal observable in the CD spectrum. However, in solution state, no CD signal could be detected. This means that in solution or in the free state, the chirality of the chiral center that is far from the chromophore cannot be transferred to the chromophore. Thus, the supramolecular chirality is induced by the gel formation process. It is strongly related to the physical state of the chiral gels. In other words, gelation-induced supramolecular chirality of a chiral gel is quite sensitive to the gel-sol transformation regulated by multiple external stimuli. The transfer of chirality from the chiral center to the chromophore was strongly dependent on the intensity and type of intermolecular or intramolecular interaction. The Cotton effect of supramolecular chirality is in accordance with the intensity of the chromophore interactions. Generally, strong intermolecular interactions will be favorable for the transfer, especially strong H-bonding and π–π stacking. Split and intense CD signals can be obtained when strong inter-chromophore stacking is adopted in gel systems.

1. M. Liu, L. Zhang and T. Wang, *Chem. Rev.*, 2015, **115**, 7304–7397.

**Andrea Pucci** asked: Can you get self-assembly using bulky solvents such as mesitylene or is aggregation prevented?

**Pengfei Duan** answered: If we use a bulky solvent, such as $CHCl_3$, $CH_2Cl_2$ or toluene, the gelator cannot self-assembly without emission. Low concentration will prevent the aggregation. However, we have not tried mesitylene. I think there should be a similar phenomenon to the toluene sample if the gelator can dissolve well in mesitylene.

**Ben Zhong Tang** commented: To follow Prof. Pucci's question, you might also check the polarity of the solvent; this is another way to tune the emission. In which solvent did you measure your CD spectra?

**Pengfei Duan** responded: We measured the CD spectra in three kinds of solvent including DMF, ethanol and toluene. This acceptor molecule showed solvatochromism properties. In polar solvents, the emission peak showed an intense red-shift which overlaps with the excitation laser at 532 nm. That is why we selected toluene as the testing solvent.

**He Tian** asked: Is your system very sensitive to oxygen and moisture? If so, how can you prepare this probe for real life applications?

**Pengfei Duan** responded: TTA-UC systems are sensitive to molecular oxygen due the extreme sensitivity of the triplet exciton. The same is true for our system. Now, we are trying to develop some oxygen-stable TTA-UC systems using such a supramolecular assembly approach. Hydrogen bonding is a nice tool to shield oxygen and we have reported several examples with oxygen-stable properties.

**Xiaohong Chen** remarked: In Fig. 5 of your paper there are 2 peaks. The first is very broad and the second is narrow - why?

**Pengfei Duan** answered: Perhaps you mean Fig 4a? This is the UC spectrum. The broad peak is the UC emission peak. The narrow one is the remaining part of the 532 nm green laser after filtering with a 532 nm notch filter.

**Nelson Leung** commented: For the upconversion emission, the emission around 450–500 nm, which overlaps with the absorption of the donor, is the emission reabsorbed by the donor? Does this affect the upconversion efficiency?

**Pengfei Duan** replied: Yes, the emission will be reabsorbed by the donor. This definitely would affect the upconversion efficiency. That is why we control the mixing ratio of the donor/acceptor with a small value. Generally, we optimize the mixing ratio of the donor/acceptor to find the best value.

**Shuizhu Wu** asked: How big can the difference be between the excitation and emission wavelength for upconversion? I think that the bigger the difference is, the more useful your system might turn out to be. Can this be tuned using the components of your system?

**Pengfei Duan** replied: Perhaps you are asking about the intensity of the anti-Stokes shift? Yes, the bigger the difference is, the more useful it is for practical applications. TTA-based UC has excellent properties: the donor and acceptor can be freely tuned, and the requirement for the excitation energy can be as low as several mW cm$^{-2}$. In this work, the anti-Stokes shift from green to blue is around 82 nm which is not a big value. Others have reported large anti-Stokes shifts from the NIR (938 nm) to the visible (570 nm) in TTA-UC systems.[1] I think there is a bright future for TTA-UC if we focus on the extension of the anti-Stokes shift.

1. S. Amemori, Y. Sasaki, N. Yanai and N. Kimizuka, *J. Am. Chem. Soc.*, 2016, **138**, 8702–8705.

**Huiqing Peng** asked: Reabsorption of the upconverted emission by the sensitizer will decrease the upconversion efficiency significantly. How can the sensitizer/emitter molar ratio be optimized for the best experimental results?

**Pengfei Duan** answered: For a new TTA upconversion system, it is hard to find the best ratio of donor/acceptor which achieves the best upconversion emission while keeping the lowest intensity of reabsorption. Due to the different absorption coefficient of donor compound, the reabsorption intensity is different. Generally, we would like to evaluate the absorption coefficient of the selected donor molecule and then compare it with a reported UC donor/acceptor pair (DPA and PtOEP are a widely reported UC pair). Then it will be clear what to fix the approximate mixing ratio of the donor/acceptor to around the reported one.

**Ming-Qiang Zhu** opened a more general discussion: We have come a long way with only organic compounds for AIE. We have a lot of organic compounds, but what will the next generation of AIE materials look like (besides TPEs, siloles)? Is it a general optical phenomenon?

**He Tian** responded: In my view, AIE materials now are not only restricted to organic compounds. There are diverse AIE systems including metal–organic frameworks, inorganic–organic hybrids, metal complexes and so on. Even for organic AIE materials, there are some new systems, such as those without classical chromophores. The AIE scope can be expanded to be as large as you can imagine. The AIE phenomenon is a general optical phenomenon for systems which have flexible and non-planar conformations. Such conformations could ensure vigorous intramolecular motions in the dispersed state and prevent $\pi$–$\pi$ stacking interactions in the aggregated state, which result in the AIE effect.

**Ben Zhong Tang** remarked: In addition to numerous organic AIE systems, a number of organometallic and hybrid AIE systems have been developed in recent years. For example, many research groups have worked on iridium complexes with AIE activity. Other examples include metallocages (*e.g.*, Peter Stang of University of Utah in USA[1]), carboranes (*e.g.*, Yoshiki Chujo of Kyoto University in Japan[2]) and POSS (*e.g.*, Jianwei Xu of IMRE in Singapore[3]). Scientists have also developed metallic AIE systems, for example, the copper clusters reported by Erkang Wang of Changchun Institute of Applied Chemistry,[4] Chao Lu of Beijing University of Chemical Technology,[5] Kaimin Shih of University of Hong Kong,[6] and Andrey L. Rogach of City University of Hong Kong.[7] AIE is thus a general phenomenon for all organic, inorganic, organometallic and hybrid luminogens. An exciting development in this area is the research on non-conventional AIE systems containing no or few aromatic rings without extended $\pi$-conjugation at the molecular level, and in particular the mechanistic study of their working mechanisms.

1. (a) X. Yan, T. R. Cook, P. Wang, F. Huang and P. J. Stang, *Nat. Chem.*, 2015, **7**, 342–348; (b) X. Yan, H. Wang, C. E. Hauke, T. R. Cook, M. Wang, M. L. Saha, Z. Zhou, M. Zhang, X. Li, F. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2015, **137**, 15276–15286; (c) M. L. Saha, X. Yan and P. J. Stang, *Acc. Chem. Res.*, 2016, **49**, 2527–2539.
2. (a) K. Kokado and Y. Chujo, *J. Org. Chem.*, 2011, **76**, 316–319; (b) R. Yoshii, A. Nagai, K. Tanaka and Y. Chujo, *Chem.–Eur. J.*, 2013, **19**, 4506–4512; (c) R. Yoshii, A. Hirose, K. Tanaka and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 18131–18139.
3. (a) H. Zhou, Q. Ye, W. T. Neo, J. Song, H. Yan, Y. Zong, B. Z. Tang, T. S. A. Hor and J. Xie, *Chem. Commun.*, 2014, **50**, 13785–13788; (b) H. Zhou, J. Li, M. H. Chua, H. Yan, Q. Ye, J. Song, T. T. Lin, B. Z. Tang and J. Xu, *Chem. Commun.*, 2016, **52**, 12478–12481.
4. (a) X. Jia, J. Li and E. Wang, *Small*, 2013, **9**, 3873–3879; (b) X. Jia, X. Yang, J. Li D. Liab and E. Wang, *Chem. Commun.*, 2014, **50**, 237–239.

5. Z. Li, S. Guo and C. Lu, *Analyst*, 2015, **140**, 2719–2725.
6. J. Liu, Q. M. Zhang, Y. Feng, Z. Zhou and K. Shih, *ChemPhysChem*, 2016, **17**, 225–231.
7. Z. Wang, B. Chen, A. S. Susha, W. Wang, C. J. Reckmeier, R. Chen, H. Zhong and A. L. Rogach, *Adv. Sci.*, 2016, **3**, 1600182.

**Eric Rivard** answered: It is worth stating that our road to AIE active phosphorescent materials was completely accidental. Our initial goal was to prepare monomers for polytellurophenes as these were expected to be promising low band gap materials for solar cells.[1] However I was lucky to have a talented postdoc, Gang He (now a professor at Xi'an Jiaotong University) who noted the AIE effect while trying to purify one of the monomers. Thus it is always a good idea to keep your eyes open and be aware of new opportunities when they arise.

1. G. He, L. Kang, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald and E. Rivard, *J. Am. Chem. Soc.*, 2013, **135**, 5360–5363.

**Yoshiki Chujo** commented: Comparing the flexibility and diversity in the molecular design of organic emissive dyes, it is still challenging to design new AIEgens *ab initio*. From this point of view, we focused on organoboron complexes and polymers and found a unique mechanism and AIE properties. Now, as we mentioned in this paper, we are aiming to establish a robust strategy towards brilliant new AIEgens.[1–5]

Moreover, development of new AIEgens would be useful for the design of stimuli-responsive solid-state emissive materials. In particular, precise control of a series of the physical properties of AIE-active materials is also challenging. In order to demonstrate one solution to this issue, we recently reported a thermally-resistant mechanofluorochromic material which can show luminescent chromism not by heating but by mechanical stresses.[6] We are also aiming to present another example having unique physical and optical properties.

1. H. Naito, K. Nishino, Y. Morisaki and Y. Chujo, *Angew. Chem. Int. Ed.*, 2017, **56**, 254–259.
2. H. Yeo, K. Tanaka and Y. Chujo, *Macromolecules*, 2016, **49**, 8899–8904.
3. K. Nishino, H. Yamamoto, K. Tanaka and Y. Chujo, *Org. Lett.*, 2016, **18**, 4064–4067.
4. S. Ito, A. Hirose, M. Yamaguchi, K. Tanaka and Y. Chujo, *J. Mater. Chem. C*, 2016, **3**, 5564–5571.
5. M. Yamaguchi, S. Ito, A. Hirose, K. Tanaka and Y. Chujo, *J. Mater. Chem. C*, 2016, **3**, 5314–5319.
6. K. Suenaga, K. Tanaka and Y. Chujo, *Chem. Eur. J.*, DOI: 10.1002/chem.201604662