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Citation for published item:
Xu, Bingjia and Li, Wenlang and He, Jiajun and Wu, Sikai and Zhu, Qianghong and Yang, Zhiyong and Wu, William and Zhang, Yi and Jin, Chongjun and Lu, Po-Yen and Chi, Zhenguo and Liu, Siwei and Xu, Jiarui and Bryce, Martin R. (2016) 'Achieving very bright mechanoluminescence from purely organic luminophores with aggregation-induced emission by crystal design.', Chemical science., 7 (8). pp. 5307-5312.

Further information on publisher’s website:
http://dx.doi.org/10.1039/c6sc01325b

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Achieving Very Bright Mechanoluminescence from Purely Organic Luminophores with Aggregation-Induced Emission by Crystal Design

Bingjia Xu,a,b Wenlang Li,a Jiajun He,c Sikai Wu,a Qiangzhong Zhub, Zhiyong Yang,a,b Yuan-Chun Wu,c Jiajun He,a,b Chongjun Jin,b Po-Yen Lu,a Zhenguo Chi,a,b Siwei Wu,a Jiarui Xu,a,b Chun Wu,c Yuan Qiangzhong Zhub and Martin R. Brycec

Although bright organic mechanoluminescence (ML) has been observed for a few luminophores with aggregation-induced emission (AIE), details of the positive effect of AIE on ML performance remain unclear and a feasible design principle for the AIE-ML compounds has not yet been presented. Herein, an effective strategy for the molecular design of efficient AIE-ML materials is demonstrated, based on tetraphenylethene (TPE) building blocks with fornyl substituents, which yield non-centrosymmetric crystal structures with prominent piezoelectric properties for molecular excitation combined with AIE features for intense emission. Following this approach, three AIE-active compounds have been developed and found to show unique ML characteristics. Furthermore, the results of single crystal X-ray analysis and density functional theory (DFT) calculations suggest that the ML performance would probably be further enhanced by creating molecules with larger dipolar moments and enhanced AIE properties.

Introduction

Mechanoluminescence (ML) which is a type of light emission induced by mechanical force on crystals has attracted increasing interest due to its special photophysical process and potential applications in displays, lighting, bioimaging and stress sensing.1 The first record on this vivid phenomenon dates back to 1605, when Francis Bacon noted that lumps of sugar being scraped at night would afford a sparkling light.2 Since then, certain inorganic compounds and organometallic complexes, such as manganese-doped zinc sulfide, Eu and Dy co-doped strontium aluminates, europium tetrakis(dibenzoylmethide) triethylammonium, ditriphenylphosphine oxide manganese bromide, and bis(methyltriphenylphosphonium) dibromochloromanganate, have been reported to show remarkable ML at room temperature.3 However, by contrast, purely organic dyes which are capable of generating intense ML are extremely scarce, and heretofore, only a few examples have been reported to display observable ML even at cryogenic temperatures or in dark.4,5 Due to their poor performance, metal-free organic compounds fail to enter discussions on practical ML applications. One of the most serious obstacles to the development of efficient purely organic ML materials is the notorious aggregation-caused quenching (ACQ) effect, which originates from strong π–π stacking interactions that greatly impede efficient emission from organic molecules.6 Consequently, bright ML is difficult to achieve in purely organic luminophores and, generally, has been regarded as a solely inorganic or organometallic property for the past four hundred years.7,8

Recently, three metal-free organic compounds, namely 10-(4-(4-(9H-carbazol-9-yl)phenylsulfonyl)) phenyl)-10H-phenothiazine (SFPC, Figure S1a), 5-(4-(1,2,2-triphenylvinyl) phenyl)thiophene-2-carbaldehyde (P4TA, Figure S1b) and 1,1,2,2-tetrakis(4-methoxyphenyl)ethane (TMPE, Figure S1c) with ML properties have been prepared by our group and by Li et al.1 The unique aggregation-induced emission (AIE) character of SFPC, P4TA and TMPE surmounted the intrinsic ACQ effect of conventional organic dyes, thus resulting in high fluorescence quantum yields (ΦH) in the solid state and intense ML even in the daylight at room temperature. These three publications also provide a new direction for the development of efficient organic ML materials by combining prominent piezoelectric properties for molecular excitation and AIE phenomena for emission. AIE luminophores (e.g. tetraphenylenethene derivatives) commonly adopt twisted conformations, which serve to effectively avoid the π–π stacking and thereby leading to dramatic emission enhancement.
As shown in Fig. 1, the molecular structure of 4-(1,2,2-
triphenylethene)benzaldehyde (p-P4A) is simple and directly
constructed by a TPE moiety and a formyl group. Under
the irradiation by UV light, the as-prepared sample of p-P4A in
the solid state emits strong bluish-green light with \( \lambda_{\text{max}} \) at 487 nm
(Fig. 2a). Since the photophysical properties of organic
molecules are correlated with their aggregation state, powder
X-ray diffraction (XRD) was carried out to determine the phase
characteristics of p-P4A. The sharp peaks in the XRD pattern
depicted in Fig. 3a unambiguously illustrate that the as-
prepared p-P4A is crystalline. Moreover, the sample of p-P4A
exhibits no other transition except an intense melting
endothermic peak in the differential scanning calorimetry (DSC)
curve (Fig. 3b). This result further confirms that the solid
powder of p-P4A is mainly composed of microcrystals that melt
at 151 °C. Intriguingly, by shearing the crystals with a spatula in
the dark, extremely strong emission was observed without the
excitation by UV light, confirming the ML character of p-P4A in
the crystalline form (Fig. 2c.i, Video S1†). Indeed, such bright
ML of p-P4A could also be clearly observed by naked eyes even

**Results and Discussion**

...
effects of these two functional fragments, single crystals of p-P_A, p-P_Ac and p-FP_A were isolated by solvent-evaporation of their solutions in a mixture of ethanol and CH_2Cl_2, and their structures solved by single crystal X-ray diffraction. The simulated XRD patterns from single crystal data of all the three luminophores are almost identical with the experimental data obtained from their crystalline powders (Fig. 3a), implying that the molecular packing modes for the as-prepared samples of p-P_A, p-P_Ac and p-FP_A are similar to the corresponding single crystals. Further study reveals that the single crystal structure of p-P_A belongs to the monoclinic system with a non-centrosymmetric polar space group of P(2)1 (Table 1). In the unit cells, two crystallographically independent conformations of p-P_A are found and interact with each other through two different kinds of C-H···O hydrogen bonds (Fig. 4b). As a result, special molecular ‘chains’ are constituted in the crystal structure. Additionally, the molecules and their counter ones show a dihedral angel of 79.68° between the phenyl rings adjacent to the formyl groups, instead of an anti-parallel packing mode, which would favor achieving the non-centrosymmetric molecular arrangement. By contrast, in the cases of p-P_Ac and p-FP_A, molecules are parallel or anti-parallel to each other and dimers are formed with the assistance of C-H···O hydrogen bonds (Fig. 4a and 4c). The highly regular molecular stacking, therefore, largely increases the symmetric elements of the crystal structures, leading to centrosymmetric and non-polar space groups for the single crystals of p-P_Ac and p-FP_A (Table 1). Obviously, the synergistic effect of the TPE and the formyl units acts as a crucial factor in yielding a non-centrosymmetric crystal structure and net dipole moment for the remarkable piezoelectric property that promotes the distinct ML emission of p-P_A by electronic discharge on the crack surface of the microcrystals.  

To further test this proposed principle, two additional luminophores of m-P_A and m-P_Ac, comprising the TPE and the formyl moieties were synthesized (Fig. 1). Their solid powders were prepared by adding concentrated dichloromethane solutions of the compounds into n-hexane under the action of ultrasound. The clear melting transitions at 136°C and 180°C in the DSC curves (Fig. 5a) and the sharp peaks in the XRD patterns (Fig. 5b) of m-P_A and m-P_Ac indicate that the corresponding crystalline morphologies. By varying the substituted position and number of the formyl group(s), m-P_A and m-P_Ac remain ML active upon grinding or shearing and their emissions are successively tuned from λ_max 472 nm to 492 nm (Fig. 5b), which are also close to their corresponding photoluminescence peaks (Fig. 5a). Both of m-P_A and m-P_Ac are stable and their ML activities could be retained even being stored in air for more than one year. Single crystal structures of these two new ML compounds adopt non-centrosymmetric molecular arrangements with polar space groups of P(2)1 and Pna(2)1, respectively (Table 1). Similar molecular stacking may thus occur in the solid powders of m-P_A and m-P_Ac because the experimental XRD patterns of these two compounds almost overlap with the simulated ones from their single crystal data (Fig. 5b). Careful analysis deciphers that the special molecular
‘chains’ polymerized by the C-H···O hydrogen bonds appear again and the molecules are all at a certain angle to their counter ones in both of the crystal structures (Fig. S3). These results are in accordance with those observed for p-PdA, thus attesting that the synergistic effect of the TPE and the aldehyde units would disorder the regularity of molecular packing and reduce the symmetry of crystal structure to provide non-centrosymmetric crystals with ML activity.

Although m-PdA, p-PdA2 and p-PdA are all ML active, their performances are different and can be readily distinguished. While p-PdA2 exhibits conspicuous ML even under daylight (Fig. 5b, Video S3 and Video S4), the emission of m-PdA could merely be discerned in dim lighting at room temperature (Video S5). Meanwhile, it should be noted that the ML brightness of p-PdA2 is slightly weaker than that of p-PdA. To gain an understanding of this aspect, theoretical calculations based on the ground state geometries in the single crystals were implemented by using B3LYP density functional theory (DFT) at the 6-31G(d, p) level to simulate the electronic transition characteristics of the compounds. The results in Fig. S4 show that all the three luminophores present an intermolecular charge transfer (ICT) from the TPE to the phenylaldehyde moiety in the solid state. Furthermore, transitions from HOMO to LUMO for p-PdA and p-PdA2 and HOMO to LUMO+1 for m-PdA with large oscillator strength (f) over 0.30 were estimated (Table S1). The dipole moments for the two conformations of p-PdA are determined to be 4.79 and 5.42 debye (D), which are both larger than that of p-PdA2 (4.78 D) and, especially, of m-PdA (3.83 D). The higher dipole moment values of the molecules would probably cause a stronger piezoelectric effect when breaking the crystals with a non-centrosymmetric molecular structure, and subsequently result in stronger excitation and higher exciton concentration on the basis of the similarly large oscillator strengths. The other hand, despite containing the typical AIE moiety of TPE that could eliminate the π-π stacking, the emission performance for m-PdA, p-PdA2 and p-PdA in the solid state might be diverse from each other. To clarify this issue, the AIE properties were investigated for these three luminophores to demonstrate the effect on ML generation.

As shown in Fig. 6a, p-PdA exhibits extremely weak emission in pure THF solution, where it is well dissolved. Nevertheless, when 95% (v/v) of distilled water is added, significant emission enhancement at around 488 nm is observed and the corresponding PL intensity increased by up to about 54-fold in comparison with the data at 0% water fraction. The UV-visible absorption profile shows Mie scattering effect for the mixtures of p-PdA with high water contents (Fig. 6b) and particles with effective diameter (E.D.) of 326 nm are observed in the mixture with 95% water (Table S2 and Fig. S7), indicating that the emission enhancement of this compound originates from the formation of nanoaggregates.13 Evidently, p-PdA is an excellent AIE chromophore that could effectively suppress the non-radiative decay to produce intense light emission in the solid state.14 Owing to AIE, the solid powder of p-PdA affords an impressive fluorescence quantum yield (ΦF) of 0.28, which is higher than most of the conventional pure organic and organometallic ML compounds. In the single crystal structure of p-PdA, detrimental species, for instance, excimers or exciplexes, caused by π-π stacking interactions have been ruled out due to the highly twisted conformations of the AIE molecules. In addition, the twisted molecular conformations have been immobilized by the multiple molecular interactions of C-H···O and C-H···π to impede the intramolecular rotation and vibration (Fig. 4 and Fig. S3). Accordingly, non-radiative relaxation would be strongly restrained, leading to a notable

### Table 1. Single crystal information of the compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Symmetry</th>
<th>Polarity</th>
<th>ML Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PdA</td>
<td>Monoclinic</td>
<td>P2(1)</td>
<td>noncentrosymmetric</td>
<td>Polar</td>
<td>Active</td>
</tr>
<tr>
<td>p-PdA</td>
<td>Triclinic</td>
<td>P-1</td>
<td>centrosymmetric</td>
<td>non-Polar</td>
<td>Inactive</td>
</tr>
<tr>
<td>p-FpA</td>
<td>Monoclinic</td>
<td>P2(1)/c</td>
<td>centrosymmetric</td>
<td>non-Polar</td>
<td>Inactive</td>
</tr>
<tr>
<td>m-PdA</td>
<td>Monoclinic</td>
<td>P2(1)</td>
<td>noncentrosymmetric</td>
<td>Polar</td>
<td>Active</td>
</tr>
<tr>
<td>p-PdA</td>
<td>Orthorhombic</td>
<td>Pna2(1)</td>
<td>noncentrosymmetric</td>
<td>Polar</td>
<td>Active</td>
</tr>
</tbody>
</table>

![Fig. 4 Molecular packing and intermolecular interactions in single crystals of p-PdA (a), p-PdA (b) and p-FpA (c).](image-url)
AIE effect for p-P4A. The remarkable emission enhancement emanated from the AIE nature and the prominent piezoelectric effect induced by the large dipolar moment in the non-centrosymmetric molecular structure, therefore makes the ML of p-P4A highly emissive under the stimulus of mechanical force. Similar results were achieved for the luminophore of p-P4A with an emission enhancement of ~29-fold from pure THF solution to the mixture containing nanoparticles with E.D. of 396 nm (λ_{max,KP}=486 nm) and a quantum yield of 0.21 in solid state. Hence, by combining the high dipolar moment value, p-P4A could also produce strong ML which is almost comparable to that of p-P4A. By contrast, for the m-P4A system only a slightly increment (~1.6 times) was recorded for the mixture (λ_{max,KP}=464 nm), indicating its relatively poor AIE property. The Φ_{PL,s} value of m-P4A was evaluated to be 0.10, which is moderate among the whole ML material family. As a result, m-P4A displays weak ML emission at room temperature upon shearing the crystals comprised of low dipolar moment molecules. As compared to the pristine samples, all the three compounds show dramatical decrease in emission intensity after grinding and the corresponding Φ_{PL,s} values of p-P4A, p-P4A₂ and m-P4A are calculated to be 0.12, 0.11 and 0.03, respectively. Although most of diffraction peaks which are consistent with the original ones remain observable in the XRD patterns of the ground samples (Fig. S8), some of the peaks become broader or even disappear. These results corroborate that the molecular packing modes of p-P4A, p-P4A₂ and m-P4A are partially altered to be amorphous state. On account of the amorphismization, intramolecular rotations and vibrations of the phenyl rings of the compounds would probably be enhanced, which therefore largely activate the non-radiative decays and reduce the Φ_{PL,s} values of the ground samples of p-P4A, p-P4A₂ and m-P4A. Obviously, although the ML activity mainly depends on the crystal symmetry of the compound, its performance would probably be enhanced by creating molecules with larger dipolar moments and more conspicuous AIE properties. From the preceding findings, it seems that all of these requirements could be fulfilled by employing a TPE moiety and one para-substituted formyl group as two of the building blocks for this molecular and crystal engineering.

Conclusions

We have presented a rational design strategy towards very bright ML from purely organic luminophores with AIE properties by introducing a TPE moiety and one para-substituted formyl group as the main components of the molecules. Under the synergistic interplay of these two units, a non-centrosymmetric crystal structure, larger molecular dipolar moment and more notable AIE performance are successfully achieved to produce a significantly enhanced ML emission upon the stimulus of mechanical force. Further study will focus on the development of more efficient ML luminogens following this precise design strategy and the applications of ML materials in optical recording and pressure sensing.

Acknowledgements
The authors gratefully acknowledge the financial support from the NSF of China (51473185), 863 Program (SS2015AA031701), the General Financial Grant from the China Postdoctoral Science Foundation (2015MS52406), the Fundamental Research Funds for the Central Universities, Guangdong Science and Technology Plan (2015B090913003 and 2015B090915003) and CSC Project (201506385012) and EPSRC (for the work in Durham).

Notes and references


