Aggregation induced emission by pyridinium–pyridinium interactions†

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Non-covalent intermolecular interactions between pyridinium subunits in a crystal-state are an efficient means to accomplish aggregation induced emission and avoid aggregation caused quenching.

Introduction

Organic luminescent molecules (luminophores) have found widespread applications in the design of optoelectronic devices and sensors. In the majority of applications, organic luminophores are either used as thin solid films or they are doped into a polymer matrix (host material). In thin films and in polymer matrices highly aggregated luminophore molecules may experience intermolecular π–π aromatic interactions. The non-covalent π–π interactions usually lead to decay of the excited-state energy of organic luminophores via non-radiative intermolecular energy transfer, thus resulting in decrease of emissive properties in the solid state. This phenomenon is well-known as aggregation caused quenching (ACQ). Due to the ACQ, the majority of organic luminophores feature considerably reduced emission or even lack of emission in the solid state, while being highly emissive in diluted solutions.

A traditional approach to minimize the detrimental intermolecular π–π stacking relies on a decrease of planarity of organic luminophores. This has been achieved by out-of-plane twisting of aromatic subunits in luminophores as well as by incorporation of steric bulk or an anionic moiety in proximity to the π-system. Combined with a restriction of intramolecular motions (to minimize the non-radiative dissipation of exciton energy), these approaches have resulted in the design of organic emitters that feature higher emission in the solid-state as compared to solution (known as aggregation induced emission or AIE). First introduced by Tang, AIE luminogens (AIEgens) have become a hot topic in materials science during the last decade, and they have found ample application in materials science. It should be noted, however, that AIEgens may lose the solid state emission if intermolecular non-covalent π–π interactions between emitter molecules can take place. Clearly, the search for a new type of interactions that would help to avoid the detrimental intermolecular π–π stacking would facilitate the development of AIEgens with improved emissive properties.

It has been demonstrated that the undesired π–π stacking can be avoided by increasing the distance between interacting π-systems in the solid state. We hypothesized that other interactions that are effective at longer distances and are more flexible with respect to mutual spatial orientation of the interacting π-systems can be utilized to avoid the undesired π–π stacking. This has led us to propose that interactions between heteroaromatic cationic π-systems can be employed in the design of solid-state luminogens (AIEgens). Interestingly, the pyridinium cation–arene π system interactions have been used by Bull and Fossey to generate luminescent responses in solution. In addition, Lu and coworkers reported a fluorescence turn-on in polymer matrices via cation–π interactions. However, to the best of our knowledge, interactions between two heteroaromatic cationic π-systems has not been used in the design of AIEgens. Herein we demonstrate that non-covalent intermolecular interactions between two neighboring pyridinium subunits in solid-state is an efficient means to accomplish the solid-state emission (Fig. 1).

Results and discussion

Synthesis of quaternary pyridinium salts 1–5

N-Benzyl pyridinium bromide 1 was obtained by alkylation of pyridine with benzyl bromide (Fig. 2). The synthesis of pyridinium carbazoles 2a and 2b involved reduction of aldehyde 6 to benzylic alcohol 7, followed by conversion to benzyl chloride and reaction with pyridine (Fig. 2). The corresponding tosylate 2b was prepared from benzylic alcohol 7 and TsCl in the presence of pyridine as a base. In addition, pyridinium carbazoles 3, 4 possessing substituents in position 4 of the pyridine ring were also synthesized to evaluate influence of steric bulk on the interaction between pyridinium subunits of neighboring molecules in the solid-state (Fig. 2). Finally, 1,4-butylene linker-
containing pyridinium carbazole 5 was prepared by double substitution of 1,4-dibromobutane with carbazole and pyridine (Fig. 2). All obtained pyridinium salts 1–5 were crystalline materials and they were characterized by $^1$H and $^{13}$C NMR spectra as well as by HRMS and IR techniques.

**Luminescence data**

UV-vis absorption spectra of 1–5 were measured in MeCN solutions (at ca. $10^{-6}$ mol L$^{-1}$ concentration) at room temperature and under ambient atmosphere. All synthesized materials displayed absorption peaks in 235–360 nm range (Fig. 3A), which were attributed to the $\pi-\pi^*$ transitions. Pyridinium salt 1 showed a narrow absorption band in MeCN solution with a maximum at 285 nm (entry 1, Table 1). Intense solid-state absorbance in the 250–350 nm region with sharply decreasing absorbance intensity above 350 nm was observed for the crystalline salt 1 (see ESI, page S10†). The salt also displayed an emission in MeCN solution (see ESI, page S9†) with photoluminescence quantum yield (PLQY) of 1.9% (entry 1, Table 1). Notably, excitation of the crystalline pyridinium salt 1 at 393 nm resulted in a solid-state emission with PLQY of 5.3% (entry 1, Table 1) and the maximum at 520 nm (see ESI, page S9†). The observed 2.8-fold increase of PLQY in the solid-state as compared to that in the MeCN solution pointed to the AIE properties of pyridinium salt 1. Next, emission properties of pyridinium salts 2–5 with attached carbazole luminophore were evaluated.

All pyridinium carbazoles 2–5 were virtually non-emissive in solutions with photoluminescence quantum yields (PLQY) below 0.1%. In sharp contrast, the solid state PLQY for pyridinium salts 2–5 were measured to be in the range from 9.7 to 18.7%. Hence, pyridinium salts featured up to 187 times increase of emission in the solid state as compared to that in MeCN solution (Table 1). These results clearly indicated that pyridinium salts 2–5 possess AIE properties. Interestingly, the solid state emission intensity was not influenced by the...
structure of the anion as evidenced by comparable solid state PLQY for pyridinium chloride 2a (entry 2, Table 1) and pyridinium tosylate 2b (entry 3). Introduction of bulky t-Bu substituent in the position 4 of pyridinium subunit did not affect the solid state PLQY of 3 (entry 4 vs. entry 3), however the corresponding 4-methyl substituted analogue 4 showed the lowest PLQY values in the carbazole series (entry 5). Finally, AIEgen 5 with a flexible butylene linker between carbazole subunit and pyridinium moiety featured only slightly reduced solid state PLQY as compared to 2b (entry 6 vs. entry 3). This is notable given a higher degree of freedom for intramolecular motions in 5 as compared to 2b due to the long alkyl chain, which may consume the excited-state through non-radiative relaxation. All AIEgens 2–5 showed a broad emission peak in the solid state with no distinctive bands except the maximum in the range of 432–520 nm (Fig. 3B). Importantly, wavelength of the solid-state emission maximum depended on the counterion in pyridinium salts 1–5. Higher energy emission peaks in the range of 432–465 nm were observed for AIEgens 2b, 3 and 4, which possess tosylate as the counter ion (Table 1, entries 3–5). In contrast, lower energy emission (503–520 nm) was measured for chloride or bromide counterion-containing AIEgens 1, 2a and 5 (Table 1, entries 1, 2 and 6). Finally, pyridinium carbazoles 2–5 displayed intense solid-state absorbance in the 250–350 nm region with sharply decreasing absorbance intensity above 350 nm. The solid-state absorbance of 2–5 was consistent with that in MeCN solution (see ESI, page S10†).

Photoluminescence behaviour of 2a in various solvent mixtures was investigated to get an additional insight in AIE properties of 2a. Lack of the emission was observed for 2a in acetonitrile (a good solvent). In contrast, enhanced emission was observed in mixtures containing high (90–95% v/v) fraction of acetonitrile.

![Fig. 3](A) UV-vis spectra of 1–5 in MeCN solutions; (B) solid state emission of 2–5; (C) emission of 2b in DMSO as a function of temperature; (D) normalized intensity of emission of 2b in the solid state and in the DMSO matrix.

Table 1 Photoluminescent properties of pyridinium salts 1–5

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>$\lambda_{\text{Abs}}, \text{nm}$</th>
<th>Solid $\lambda_{\text{Em}}, \text{nm}$</th>
<th>Solution $\phi$ (%)</th>
<th>Solid $\phi$ (%)</th>
<th>$\alpha_{\text{AIE}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>258</td>
<td>520$^a$</td>
<td>1.9</td>
<td>5.3</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>241, 290, 325, 337</td>
<td>505$^b$</td>
<td>&lt;0.1</td>
<td>17.3</td>
<td>&gt;173</td>
</tr>
<tr>
<td>3</td>
<td>2b</td>
<td>264, 295, 324, 337</td>
<td>432$^b$</td>
<td>&lt;0.1</td>
<td>18.7</td>
<td>&gt;187</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>260, 294, 325, 337</td>
<td>465$^b$</td>
<td>&lt;0.1</td>
<td>18.5</td>
<td>&gt;185</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>240, 292, 324, 337</td>
<td>442$^b$</td>
<td>&lt;0.1</td>
<td>9.7</td>
<td>&gt;97</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>263, 292, 330, 343</td>
<td>503$^b$</td>
<td>&lt;0.1</td>
<td>15.9</td>
<td>&gt;159</td>
</tr>
</tbody>
</table>

$^a$ Excited at 393 nm. $^b$ Excited at 325 nm.
of Et₂O (a poor solvent) in MeCN (see ESI, page S13†). The
dynamic light scattering (DLS) measurements indicated that
pyridinium salt 2a did not form aggregates in solvent mixtures
that contained less than 90% of Et₂O in acetonitrile (see ESI,
page S13†). Notably, the lack of emission was observed for 2a in
these solvent mixtures. In contrast, the formation of aggregates
could be observed even by the naked eye if 90–95% (v/v) of Et₂O
in acetonitrile was used as the solvent. In the latter case, the size
of aggregates was larger than 10 μm, thus exceeding limits of
DLS measurements. The apparent correlation between the
formation of aggregates and luminescence provided an addi-
tional support for AIE properties of pyridinium salt 2a.

We have also examined whether AIE properties of pyridinium
salts 1–5 originate from restriction of intramolecular rotation
(RIR) phenomena. To this end we measured a relationship
between emission of 2b in DMSO solution and temperature in
the range from 293 K to 208 K (Fig. 3C). A solution of 2b in DMSO
did not display observable emission at 293 K. Importantly, the
emission increase could not be determined after freezing of the
DMSO solution of 2b, as well as upon further cooling to 238 K.
The emission only started to appear at temperatures below 238 K
and the intensity increased considerably at 208 K (Fig. 3C). Lack
of the emission for 2b in the DMSO matrix points against the RIR
mechanism as the origin of AIE properties of 2b, because
considerable enhancement of the emission in solid matrices is
usually observed for most of AIEgens that benefit from RIR
effect. Furthermore, the emission peak for 2b in frozen DMSO
matrix showed bathochromic shift as compared to that in the
solid state (Fig. 3D). Finally, the solid state emission intensity for
crystalline 2b remained unchanged in the temperature range
from 293 K to 193 K. These data provide evidence that the
lumogens 1–5 show AIE properties in crystalline form.

### Single crystal X-ray analysis

Single crystal X-ray analysis of luminogens 2–5 provided
important insight into intermolecular interactions that result in
AIE properties (Table 2). Single crystals of pyridinium salts 2–5
suitable for X-ray crystallography could be obtained by vapor
diffusion from various solvents systems such as acetone/EtOH,
DCM/hexane, EtOAc/MeCN, toluene/DCM or Et₂O. In a crystal
lattice pyridinium salts 2a, 2b, 3 and 5 feature intermolecular
π–π interactions between the charged pyridinium rings. This
is evidenced by a strictly parallel off-center orientation of
neighboring pyridinium rings with the distance between them
spanning a range from 3.686 Å (for 5) to 4.211 Å (for 2a; see
Table 2). In contrast, pyridinium salt 4 does not have the π–π
interactions between the charged pyridinium rings. Instead,
interactions between pyridinium ring and 1,4-disubstituted
phenylene moiety can be observed for 4 as evidenced by a rela-
tively close distance (from 3.803 Å to 4.027 Å) between the two
nonparallel-oriented π-systems (Table 2). It should be noted
that pyridinium salt 4 demonstrated lower PLQY as compared
to other AIEgens 2a, 2b, 3 and 5 (see Table 1), suggesting that
pyridinium–pyridinium interactions are important to achieve
greater AIE properties in the crystalline state.

In addition to the intermolecular pyridinium–pyridinium
interactions in the crystal lattice of 2b, the aromatic system
of tosylate anion is positioned in a non-parallel off-center
orientation with respect to pyridinium ring (3.843–4.186 Å distance,
see ESI, page S9†). However, the latter interaction apparently
does not influence the AIE properties of 2b, as evidenced by
similar PLQY values for 2b and the analogous AIEgen 2a, pos-
sessing chloride as the counter-ion (see entries 2 and 3, Table 1).
The other tosylate-containing AIEgens 3 and 4 do not show the
face-to-face interactions between pyridinium cation and π-
system of the tosylate anion. Hence, these data demonstrate that the crystal-state AIE effect can be achieved using chloride, bromide and tosylate as the counter-ion for pyridinium. Importantly, nature of counter-ion influences the solid-state emission maximum of AIEgens. Thus, change of the counter-ion in AIEgen 2 from tosylate (2b) to chloride (2a) resulted in a noticeable bathochromic shift of more than 70 nm (Fig. 3B). The dependence of the solid-state emission maximum on the nature of the counter-ion simplifies the design of AIEgens with the desired emission wavelength.

Conclusions

All synthesized pyridinium salts 1–5 demonstrate AIE properties with up to 187 times emission increase in the crystal-state as compared to solution. Lack of emission for 2b in solution and frozen DMSO matrix (solid amorphous state) speaks against the RIR effect as the origin of the AIE properties for pyridinium salt 2b. Single crystal X-ray analyses provide clear evidence for the presence of non-covalent intermolecular pyridinium–pyridinium and pyridinium–π interactions in the crystal-state of AIEgens 2–5. Consequently, crystal-state AIE effect can be attributed to the intermolecular π+-π− and π−–π interactions involving pyridinium cations. Hence, non-covalent interactions between two neighboring pyridinium subunits in a crystal-state are an efficient means to accomplish AIE. The nature of counter-ion in pyridinium salts 2–5 does not affect emission efficiency (PLQY) of the crystal-state AIEgens, however, the counter-ion does influence the crystal-state emission maximum of AIEgens. The use of the non-covalent pyridinium–pyridinium or pyridinium–π interactions in the design of AIEgens is alternative and complementary approach to routinely used means to avoid the ACQ effect. Further studies on the design of the crystal-state AIEgens based on interactions between cationic π systems will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References


15. 9-(4-Benzylphenyl)-9H-carbazole 10 (see ESI, page S7†), an analog of 2a,b with benzene ring instead of the pyridinium subunit does not possess AIE properties. It features high solution-state emission (39.9% PLQY) and reduced solid-state emission (35.5% PLQY). For photophysical properties of 10, see ESI†.