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Unusual Alternating Crystallization-Induced Emission Enhancement Behavior in Non-Conjugated ω-Phenylalkyl Tropylium Salts

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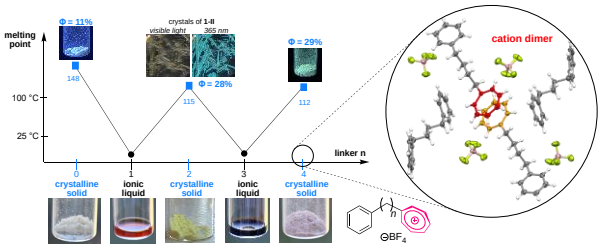


ABSTRACT: The alternating physical properties, especially melting points, of α,ω-disubstituted *n*-alkanes and their parent *n*-alkanes had been known since Baeyer's report in 1877. There is, however, no general and comprehensive explanation for such phenomenon. Herein, we report the synthesis and examination of a series of novel ω-phenyl *n*-alkyl tropylium tetrafluoroborates, which also display alternation in their physicochemical characters. Despite being organic salts, the compounds with odd numbers of carbons in the alkyl bridge exists as room temperature ionic liquids. In stark contrast to this, the analogues with even numbers of carbons in the linker are crystalline solids. These solid non-conjugated molecules exhibit curious photoluminescent properties, which can be attributed to their ability to form through-space charge-transfer complexes to cause crystallization-induced emission enhancement. Most notably, the compound with the highest photoluminescent quantum yield in this series showed an unusual arrangement of carbocationic dimer in solid state. A combination of XRD analysis and *ab initio* calculation revealed interesting insights into these systems.

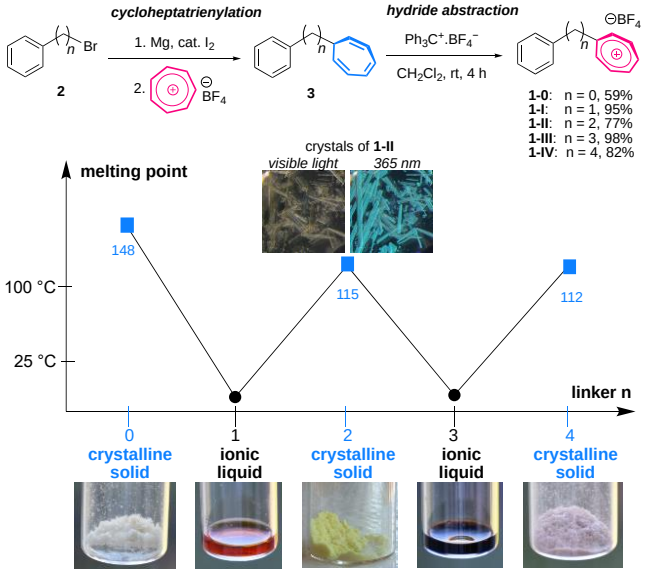
INTRODUCTION

Charge-transfer organic dyes have been extensively studied in the past decades for applications from sensing and biological staining to photocatalysis, and more recently organic light-emitting diodes (OLEDs) to dye-sensitised solar cells.[1] Fluorescent organic dyes are of particular interest as their easily tunable structures and biocompatibility make them attractive frameworks for the abovementioned applications.[2] Most of traditional organic fluorophores are conjugated systems and conjugation of extended π-frameworks was once deemed crucial for fluorescence.[3] However, the recent recognition and developments of aggregation-induced emission (AIE)[4] in particular or clusterization-triggered emission (CTE)[5] fluorescent materials in general have identified numerous non-conjugated frameworks that exhibit visible emission in aggregates or solid states. These clusteroluminogens can be generally divided into categories of metal complexes, polymeric materials or small organic molecular systems.[5] The latter, being more structurally well-defined and synthetically accessible, has an important role in this emerging field as it can act as the platform for theoretical and experimental studies to fully understand why non-conjugated fluorophores emit light and to improve their performance by structural design.

From our previous work in chemistry of tropylium ions,[6] we have reported the use of non-benzenoid cationic tropylium moiety as a convenient electron-deficient building block for photoactive materials.[7] Tropylium ion has also been long known to form inter- or intra-molecular π-π complexes with phenyl rings in arenes.[8] The phenyl group is a fundamental building block for fluorescent materials, even in isolated positions.[9] Thus, it would be fascinating to install a tropylium ion in conjunction with a phenyl ring in a non-conjugated arrangement so that they can interact with each other via through-space charge-transfer[10] to obtain novel clusteroluminogenic molecules. Such simple molecular frameworks can also be easily computationally simulated and studied as model systems to gain more insights into the molecular dynamics of CTE.

SYNTHESIS AND PHYSICAL PROPERTIES

Thus, a series of novel ω-phenyl *n*-alkyl tropylium salts were synthesized in two steps from commercially available starting materials **2** (Scheme 1).[11] The first step was a direct cycloheptatrienylation reaction of the ω-phenyl *n*-alkyl magnesium bromide. The second step was a hydride abstraction at the 7-position of the newly formed cycloheptatrienes **3** to convert it to the tropylium salts **1**. This synthetic sequence was relatively high yielding and required a minimal amount of effort on product purification, making it practical for large scale synthesis. Most of compounds **1** were relatively stable for quick handling under ambient conditions in the laboratory and long-term storage under argon atmosphere and refrigerated conditions. Compounds **1-I** and **1-III** appeared to be dark-orange or dark-brown colored (Scheme 1) due to trace amounts of inseparable impurities.



Scheme 1. Synthesis of ω-phenyl *n*-alkyl tropylium salts.

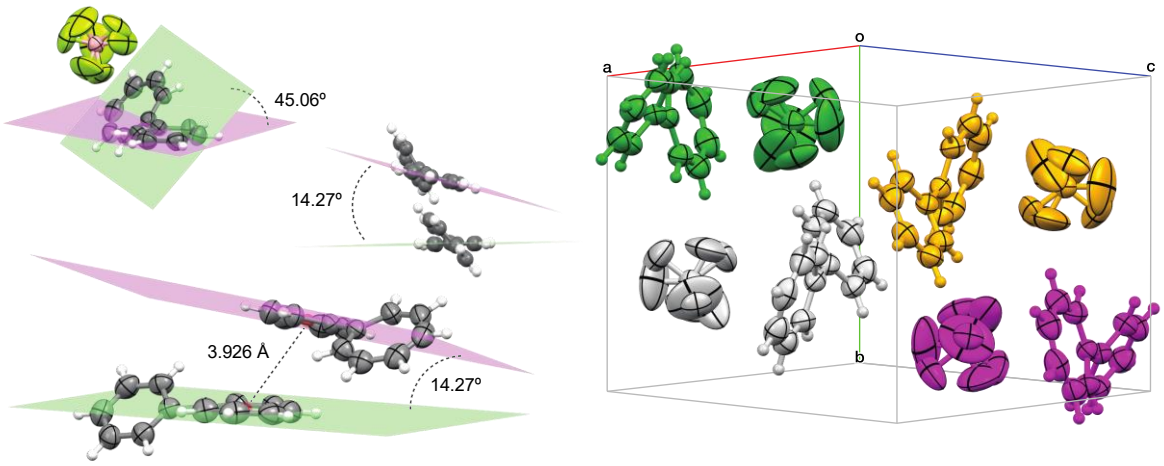
Intriguingly, this series of five tropylium salts showed an alternating behavior in their melting points. The salts with odd numbers of carbon atoms in the linkers (**1-I** and **1-III**) were highly viscous oils at 25 ºC, making them room-temperature ionic liquids. Surprisingly, differential scanning calorimetry analysis for **1-I** and **1-III** showed that there were no phase change for these two compounds in the range of ±70 ºC (see pages S12 and S14 in the SI).[11] In contrast, the salts having even numbers of carbons in the alkyl chains (**1-0**, **1-II** and **1-IV**) were crystalline solids with melting points higher than 100 ºC (Scheme 1), unambiguously excluding them from ionic liquids by definition. The melting points seemed to decrease in the even-numbered linker series as the length between the tropylium moiety and the phenyl terminal increased, despite the increasing molecular weights (Scheme 1). This interesting alternation in melting points resembles the textbook phenomenon in α,ω-disubstituted *n*-alkanes and their parent *n*-alkanes,[12] but the difference was much more amplified in this series. The difference in melting points for ω-phenyl *n*-alkyl tropylium salts **1** containing an even or odd number of CH_2 in the linker could be affected by the ability to form crystal from monomer (indicating by free binding energy), geometry of monomer in the crystal environments, and packing force (see the Computational Studies section for more details). In the recent years, this phenomenon has been observed for a range of ionic liquids and organic structures,[13] however only a few of them displayed photoactivity.[14] Our crystalline salts with even-numbered linkers are photoluminescent, as can be seen from the representative photos of **1-II** crystals under visible and UV light (Scheme 1).

CRYSTAL STRUCTURES OF 1-0, 1-II AND 1-IV

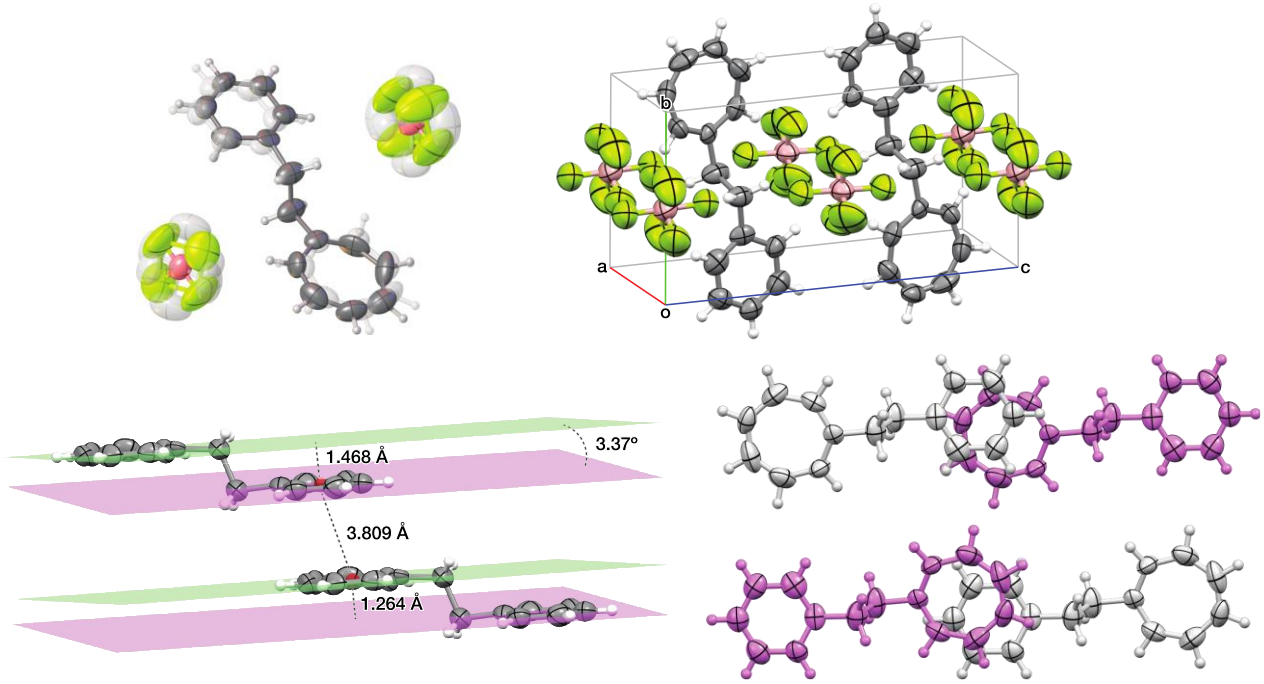
To obtain insights into the interesting alternating behavior of this compound series, we grew crystals of **1-0**, **1-II** and **1-IV** to examine their X-ray single crystal structures. While it was trivial to grow crystals of **1-0** and **1-IV**, **1-II** proved to be a lot more difficult to obtain a single crystal suitable for XRD analysis. Crystal structures of **1-0** and **1-II** are depicted in Figures 1a-1b, respectively. The crystal structure of **1-IV** is depicted in Figure 2.

As expected, the tropylium rings in both **1-0** and **1-II** were essentially planar[15] and shaped as perfect heptagons, indicating that they retain their unique non-benzenoid aromaticity (Figure 1). In the crystal structure of compound **1-0**, the tropylium ring (Trop, light green plane) is twisted 45º out of the plane of the phenyl ring (Ph, light purple plane). The tropylium rings also appear to be participating in intermolecular π-stacking interactions with the phenyl rings of adjacent molecules, with their respective planes twisted by ~14º and a distance between 3.235-4.014 Å (3.926 Å between the two centroids, Figure 1a), which is within the normal range for arenes.[16]

As mentioned above, obtaining a suitable crystal of compound **1-II** proved more challenging, as it often led to clusters of crystals. Eventually, a suitable crystal was obtained from low temperature recrystallization from dichloromethane/diethyl ether, however the structure refinement necessitated modelling of significant orientational disorder of the 2-phenylethyl tropylium ion as well as the BF_4 counterions over two positions (Figure 1b). In the crystal structure of compound **1-II**, the centroids of the two aromatic cycles, Ph and Trop, unusually lie on approximately the same axis plane made by the two carbons of the alkyl linker (Figure 1b). The planes containing Ph and Trop are almost parallel to each other with an angle between the planes of only 3.4º, and an intramolecular distance between 1.264-1.468 Å. More notably, the intermolecular distances between the centroids of the Ph or Trop rings of one molecule to the Trop or Ph rings of the adjacent molecule are 3.387 and 3.433 Å, respectively. The Ph-centroid to Trop-centroid distance is 3.809 Å. It clearly suggests that there are head-to-tail (Trop-to-Ph) π – π stacking interactions between **1-II** molecules in the crystalline solid state. Presumably, these interactions allow through-space charge transfer, leading to the CIEE phenomenon in **1-II**, as discussed in the next section.



(a) Crystal structure of **1-0** showing 50% probability ellipsoids for all non-hydrogen atoms; bottom-left: BF_4 omitted for clarity.[17]



(b) Crystal structure of **1-II** showing 50% probability ellipsoids for all nonhydrogen atoms; top-left: asymmetric unit depicting orientational disorder over two positions for both the 2-phenylalkyl tropylium ion as well as the BF_4 anion. Only one of the orientations is depicted thereafter (the second orientation is omitted) for clarity; bottom: BF_4 omitted for clarity.[18]

Figure 1. Crystal structures of **1-0** and **1-II** with relevant distances and angles. The mean planes of the tropylium rings and the phenyl rings are green and purple colored, respectively.

On the other hand, the crystal structure of **1-IV** revealed surprising features. Similar to **1-0** and **1-II**, the tropylium ion is planar, and like **1-II**, the centroids of Ph and Trop lie on approximately the same axis plane made by the four carbons of the alkyl linker (Figure 2). However, the planes containing two aromatic cycles, Ph and Trop, in the same molecule are not parallel to each other but instead are twisted by ~20º. Most importantly, the intermolecular interactions within the crystal lattice revealed some astonishing results. Two tropylium ions from two adjacent molecules are perfectly parallel to each other and appeared to be in an offset head-to-head (Trop-to-Trop) π – π stacking arrangement. It is highly unusual that the electronic repulsion forces seem to have little or no impact on the crystal packing, with an extraordinarily close plane-to-plane distance of 3.455 Å, typical of π-stacking in neutral arenes.[16] This is similar to the close stacking of the trialkylaminocyclopropenium (TAC) cationic dimer reported by Crittenden, Curnow and coworkers,[19] which had a distance between centroids of the cyclopropenium dimers around 3.23 Å. The small centroid distances in Crittenden and Curnow's case were attributed to the stabilization of the positive charges by the exocyclic amino groups and the rotational offset of 60° between the two deltic frameworks. However, our compound **I-IV** does not have the capacity to delocalize the positive charge over amino-groups, hence this lattice arrangement is remarkable. Also evident in the crystal structure is a C-H – π interaction, at a distance of approximately 2.680 Å, between the tropylium C-H and the π-system of a phenyl group on the adjacent molecule (Figure 2). We

believe that the dimeric head-to-head tropylium π-π stacking interactions are possible due to the charge stabilization through these CH – π interactions as well as the electrostatic bridges by BF_4^- counter ions. These networks of weak short-range interactions, as depicted in Figure 2, presumably lead to efficient through-space charge transfer, causing the CIEE phenomenon in **1-IV** as discussed later.

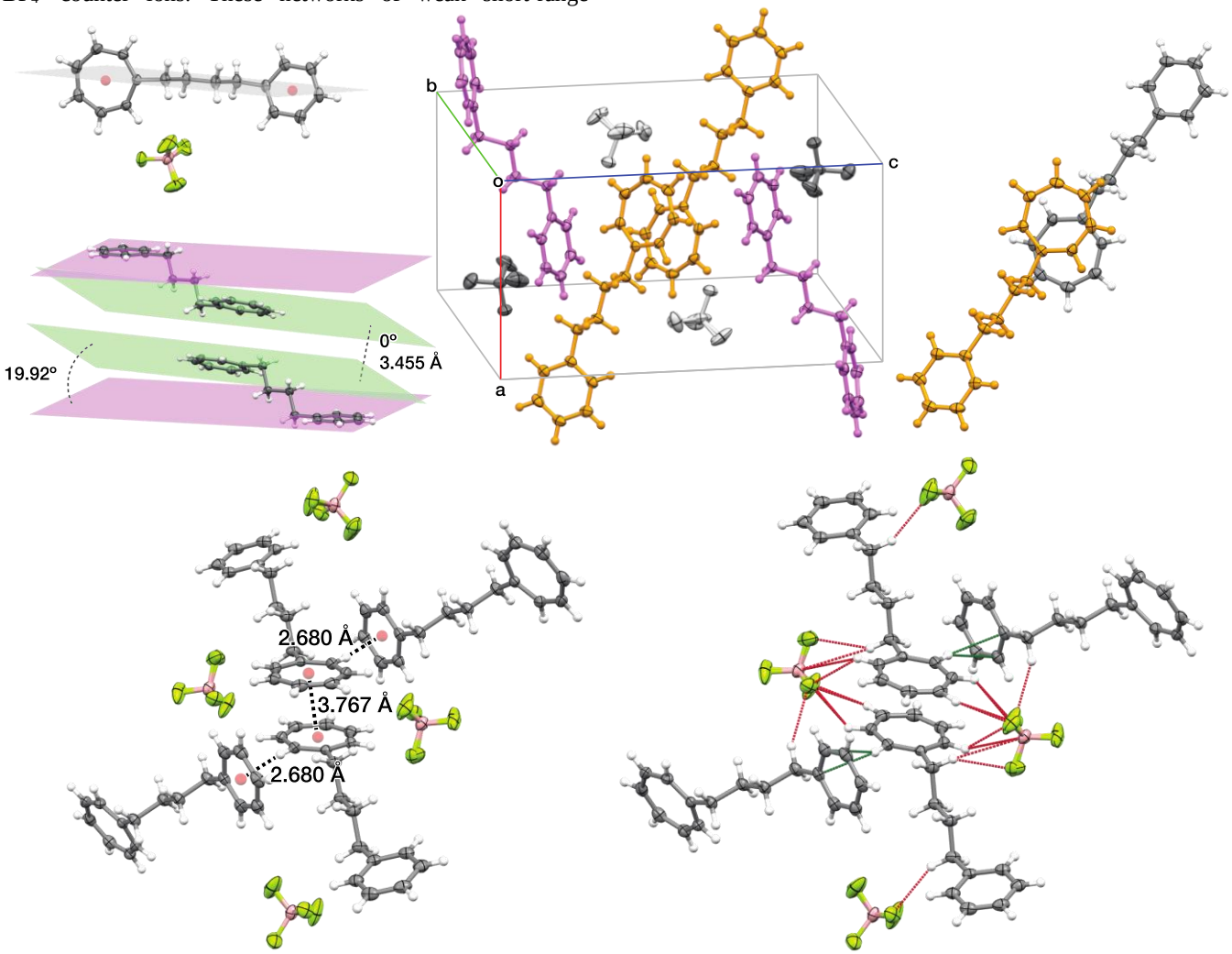


Figure 2. Crystal structure of **1-IV** showing 50% probability ellipsoids for all nonhydrogen atoms with relevant distances and angles displayed. The mean planes of the tropylium rings and the phenyl rings are green and purple colored, respectively. Short-range interactions (defined as distances less than the sum of the van der Walls radii) between depicted molecules are displayed by dashed red lines. C-H – π interactions are displayed by dashed green lines. Top: BF_4 omitted for clarity.[20]

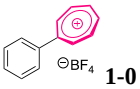
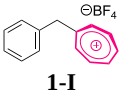
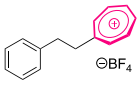
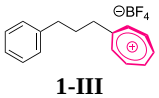
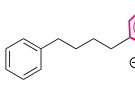
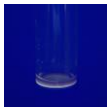
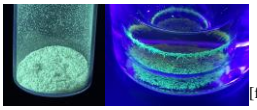
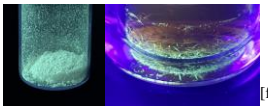
PHOTOPHYSICAL PROPERTIES

We subsequently studied the photophysics of these ω-phenyl *n*-alkyl tropylium salts, with the expectation to observe a similar alternating behavior. Indeed, the compounds odd numbers of carbon atoms in the linkers (**1-I** and **1-III**) did not exhibit any photoluminescence in both neat or solution forms. On the other hand, the crystalline solids **1-0**, **1-II** and **1-IV** were light blue luminescent under 365 nm UV irradiation (Table 1). However, **1-II** and **1-IV** were almost completely non-luminescent in solution forms, as can be seen in the photo of their crystals inside recrystallization mother liquors (Table 1), suggesting that they are probably clusteroluminogenic molecules. It should be noted here that the photographed mother liquors still contained **1-II** and **1-IV** at more than 10 mM concentration. Also, these compounds are relatively photo-stable (see photostability studies, pages S24-S44 in the SI). A further study embedding these two compounds on polymethylmethacrylate (PMMA) matrix did not show any detectable luminescence either (see page S18 in the SI for further details). Therefore, it can be concluded that **1-II** and **1-IV** have their emission induced or enhanced by crystallization. The excitation spectrum of the crystal and PMMA film samples were a reasonable match to the corresponding absorption spectra (see Figure S4 in the SI).

Examination of the distance and orientation of tropylium and phenyl groups in the crystal structures of **1-II** and **1-IV** supports these photophysical observations (Figure 1b and Figure 2). The crystal structure of **1-II** revealed intermolecular π–π interaction between tropylium and phenyl units. Strong charge transfer interaction is expected between the electron-rich phenyl and electron-poor tropylium units in this crystal structure arrangement. The UV-vis absorption and photoluminescence spectra of crystal samples of these compounds (Figure 3) show that absorption intensities are correlating to charge transfer

interactions in their crystal structures. The absorption peaks at 400 and 460 nm for the **1-II** crystal sample (Figure 3) can be assigned to charge transfer interactions due to the parallel-displaced π-stacking of the Ph and Trop rings (Figure 1b). The crystal structure of **1-IV** revealed an edge to face interaction (T-shaped π-stacking) between the phenyl and tropylium rings, making the charge transfer interaction weaker for **1-IV** compared to **1-II** (Figure 2). This corresponds with the less prominent absorption features of the **1-IV** crystal sample. Both **1-II** and **1-IV** crystal samples were highly photoluminescent with emission peaks at 490 and 494 nm and PLQY of 28% and 29% respectively. The photoluminescence lifetime for both **1-II** and **1-IV** are rather long at 26.8 ns and 56.8 ns, respectively. These long lifetimes, along with the fact that both compounds are non-emissive in solution, indicate the emission in crystals is a result of intermolecular charge transfer species.[5]

Table 1. Photophysical properties of ω-phenyl *n*-alkyl tropylium salts **1**.

Photophysical Properties[a]	 **1-0**	 **1-I**	 **1-II**	 **1-III**	 **1-IV**
λ_{abs} (solution[b]) nm	274, 384	282, 340	296, 345	282, 345	296
$\lambda_{em}/\lambda_{ex}$ (solution) nm	478/384	564/340	574/345	565/345	-[c]
PLQY (solution)	5.0 ± 0.1%	-[c]	-[c]	-[c]	-[c]
Lifetime (solution)	0.97 ns	-[d]	2.56 ns	-[d]	1.91 ns
Solid/neat oil form under 365 nm UV			 [f]		 [f]
λ_{abs} (crystal) nm	380	-[e]	314, 400, 460	-[e]	300, 380
$\lambda_{em}/\lambda_{ex}$ (crystal) nm	470/380	-[e]	490/380	-[e]	494/380
PLQY (crystal)	11 ± 1%	-[e]	28 ± 2%	-[e]	29 ± 2%
Lifetime (crystal)	1.95 ns	-[e]	26.8 ns	-[e]	56.8 ns

[a] See the experimental Supporting Information for UV-vis and emission spectra, fluorescence decay profiles and further technical details; [b] All solutions were in CH_2Cl_2 solvent; [c] Value was too low to be detected or negligible; [d] Value was not measured. [e] No crystal obtained. [f] Photo of crystals growing in mother liquor DCM/Et_2O.

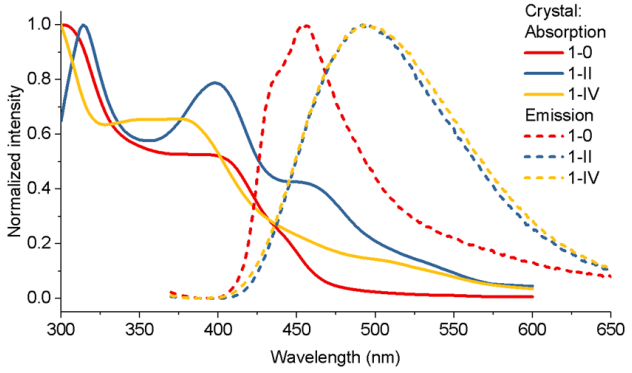


Figure 3. Normalized UV-vis absorption and photoluminescence (350 nm excitation) spectra of crystal samples of **1-0**, **1-II** and **1-IV**.

Interestingly, compound **1-0** was luminescent in solution and as a crystalline solid, with PLQY of 5% and 11% respectively (Table 1). The excitation spectrum of **1-0** in CH_2Cl_2 and in crystal form showed a good match with the corresponding absorption spectrum (Figures S2 and S4 in the SI). Compound **1-0** also suffered from aggregation-caused quenching in solution state (see page S23 in the SI for further details), so its emission in solid state is due to crystallization-induced emission enhancement (CIEE) rather than the typical AIE phenomenon. Compound **1-0** was also luminescent in PMMA matrix with emission peak at 430 nm and PLQY of 11% (see Figure S3 in the SI). There is significant spectral variation between the solution, crystal and PMMA samples of **1-0** which can be attributed to molecular rigidification, aggregation and crystal packing effects. The photophysical behaviour differences between **1-0** and the other tropylium salts can be attributed to the fact that **1-0** is the only compound with a direct biaryl-type phenyl-tropylium C-C bond. In CH_2Cl_2 solution, compound **1-0** has an absorption peak at 384 nm which can be assigned to the π–π* transition of the conjugated phenyl-tropylium structure (Figure S1 in the SI).[21] The solution spectrum of compounds **1-I**, **1-II** and **1-III** showed absorption peak at 340, 345 and 345 nm respectively with decrease in absorptivity as the alkyl spacer length increased (see Figure S1 in the SI). This is a strong indication that this absorption feature is a result of through-space intramolecular charge transfer. Absorption peaks at similar wavelengths was reported in tropylium ion-aromatic hydrocarbon charge-transfer complexes in solution.[22]

Thus, within a simple series of ω-phenyl *n*-alkyl tropylium salts, we have observed an interesting alternating behavior of physical and photophysical properties. The even-numbered linker analogues (**1-0**, **1-II** and **1-IV**) are novel clusteroluminogens with CIEE phenomenon, while the odd-numbered linker compounds (**1-I** and **1-III**) are novel room-temperature ionic liquids. To the best of our knowledge, **1-I** and **1-III** marked the first examples of the non-benzenoid aromatic tropylium ion in

ionic liquids, despite the relevant cyclopropenium ionic liquids having been known for years.[19, 23]

COMPUTATIONAL STUDIES

It was very curious as to why the even-numbered linker ω-phenyl *n*-alkyl tropylium tetrafluoroborates are crystalline solid and clusteroluminogenic while the odd-numbered linker analogues are quite the opposite. Is this just a coincidence or does linker chain length play an important role in dictating the properties of these simple clusterlumigenic molecules? In order to get more insights into interactions at each species, *ab initio* calculations on the possibility to form dimers of these compounds were carried out at the DLPNO-CCSD(T)/cc-pVTZ//M06-2X–D3/def2-TZVP level of theory (see the computational part of the SI for more details). The optimized structures for head-to-head (i.e., Trop-to-Trop, denoted as suffix **HH**) and head-to-tail (i.e., Trop-to-Ph, denoted as suffix **HT**) dimers of phenylalkyl tropylium salts **1** are shown in Figure 4. In all dimers, various noncovalent interactions are found, including π/CH–π interactions, C-H···F hydrogen bonds, and through-space electrostatic interactions (see Figure S17, S18, S19 in the SI for noncovalent analysis, molecular electrostatic potentials, and C-H···F distances in all dimers, respectively). These interactions could facilitate the formation of these dimers indicated by large binding free energy ΔG_{bind} values. It should be mentioned that we have also optimized tail-to-tail, i.e., Ph-to-Ph, dimers (see Figure S20 the SI). However, these dimers are calculated to be unfavourable, as indicated by their positive ΔG_{bind} values.

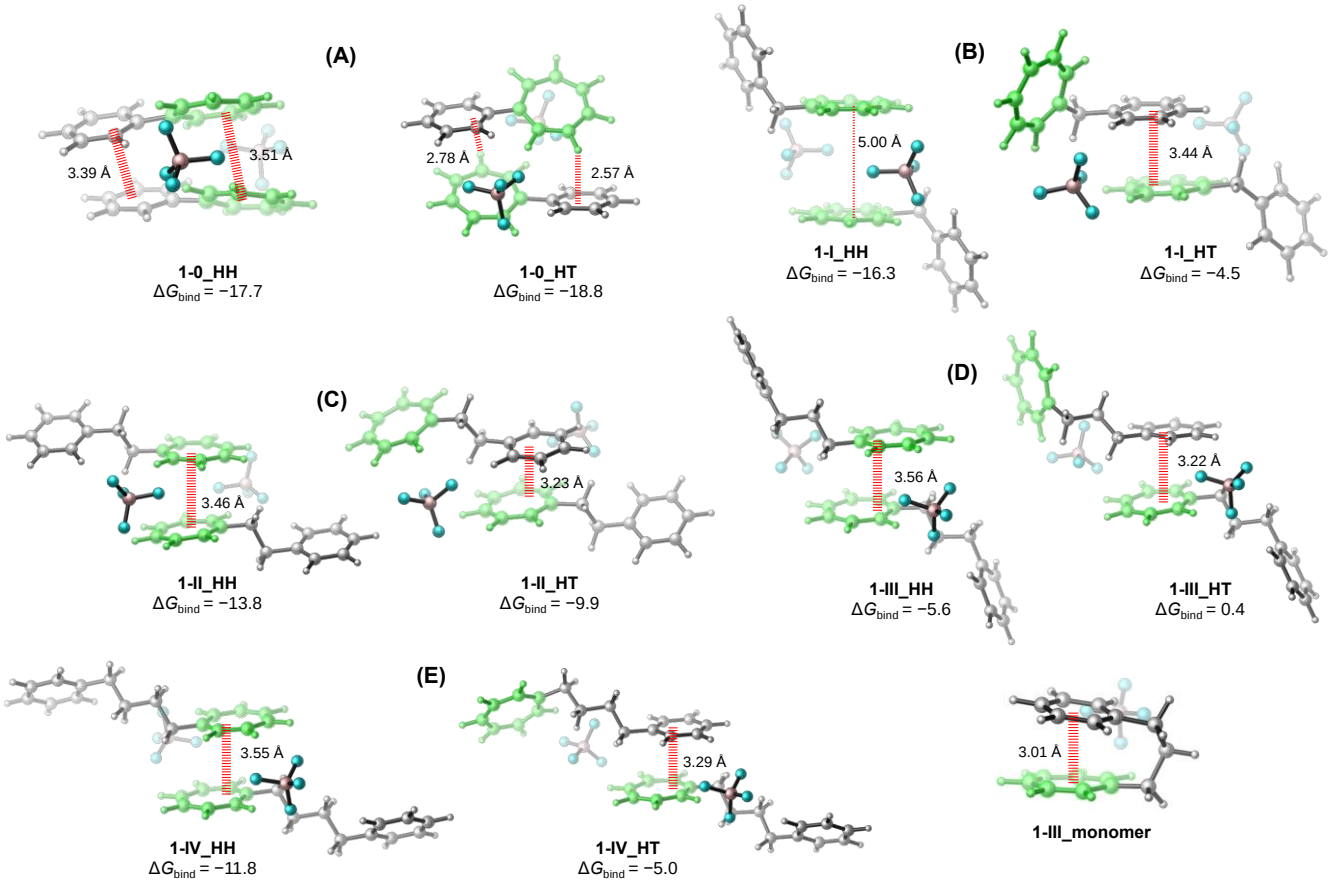


Figure 4. Optimized structures for the head-to-head and head-to-tail dimers of (A) **1-0**, (B) **1-I**, (C) **1-II**, (D) **1-III**, and (E) **1-IV**. Tropylium moieties are highlighted in green. **1-0_HT**, **1-II_HT**, and **1-IV_HH** are dimers that were found in the corresponding crystal structures. The π/CH–π distances are calculate from the ring centroids to the corresponding ring planes. Binding free energy is calculated as $\Delta G_{bind} = G_{dimer} - 2\times G_{monomer}$ (in kcal/mol).

For the phenyl tropylium salt **1-0**, because of stronger binding energy, the head-to-tail arrangement is favorable. Because of the strong binding affinity (ΔG_{bind}=−17.7 kcal/mol), the head-to-head arrangement of **1-0** (**1-0_HH**) is also possible. However, the probability to observe this structure is calculated to be much smaller than the head-to-tail arrangement. Because of the electrostatic repulsion between tropylium and tropylium group, the ring – ring distance in head-to-head dimers are longer than that in head-to-tail complexes, which suggests that the ring – ring dispersion in head-to-tail dimers is stronger than that in head-to-head complexes. Interestingly, because of the electron-withdrawing inductive effect of the benzyl group, the natural atomic charge (NPA), which is derived from natural atomic orbitals,[24] of tropylium moiety in **1-I** is calculated to be 0.90. The calculated NPA charge is higher than that in other phenylalkyl tropylium salts, resulting in a very long ring – ring distance in **1-I_HH** (~5.00 Å, Figure 4B) in order to relieve electrostatic repulsion between tropylium – tropylium groups. The long ring – ring distance in **1-I_HH** could lead to low packing force for **1-I**, explaining the very low melting point of the room-temperature ionic liquid **1-I** (Scheme 1).

For the phenylethyl tropylium salt **1-II**, although the free binding energy of head-to-head dimer **1-II_HH** is higher than that of the head-to-tail dimer **1-II_HT** (Figure 4), the head-to-tail arrangement is observed in solid state (Figure 1b). This result suggests that the ability to bind other phenylalkyl tropylium molecules to generate larger complexes, including trimer and tetramers, is important and should be considered. Thus, we carried out representative calculations for the tetramer complexes obtained from head-to-head or head-to-tail dimers of **1-II**, which are depicted in Figure 5 below. The crystal packing of **1-II** was likely controlled by the formation of more complicated clusters than these tetramers; however, these systems calculated in Figure 5 can serve as simplified models. In the tetramer generated from **1-II_HH**, a combination of head-to-head and tail-to-tail π-π stackings was observed. On the other hand, in the tetramer generated from **1-II_HT**, only head-to-tail arrangement was possible. Because of the unfavorable of tail-to-tail π-π stacking (see Figure S20 in the SI), the tetramer generated from **1-II_HH** is less favorable than that obtained from **1-II_HT**, leading to the preference of head-to-tail arrangement in crystal structure of **1-II**.

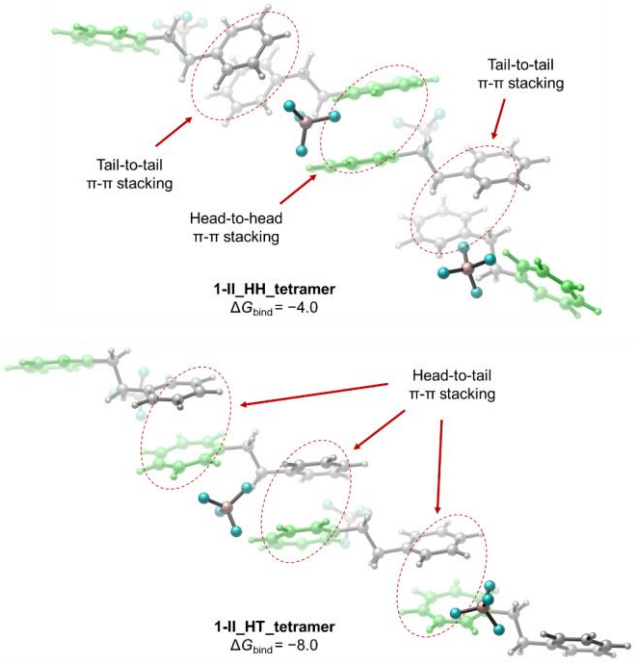


Figure 5. Tetramers of **1-II** generated from (top) head-to-head dimer and (bottom) head-to-tail dimer. $\Delta G_{bind} = G_{dimer} - 4\times G_{monomer}$ (in kcal/mol).

In the case of **1-III**, we found that the optimization of its structure led to a strong intramolecular π–π interactions between the tropylium and the phenyl rings in its monomeric form (Figure 4D). This is a unique feature of **1-III** as no other member of this series has the right linker length for such intramolecular interaction. It led to low binding free energies of **1-III_HH** and **1-III_HT** dimeric forms (Figure 4D), disfavoring the dimerization of **1-III**. This is probably the reason why **1-III** is also an ionic liquid at room temperature. For **1-IV**, because the head-to-head arrangement (**1-IV_HH**) is ~ 6.8 kcal/mol lower in energy than the head-to-tail arrangement (**1-IV_HT**), the **1-IV_HH** is a lot more favourable, which is consistent with our XRD data.

The general shapes for each monomer in phenylalkyl tropylium salts dimers are shown in Figure 6. In the species that have an even number of CH_2, i.e., **1-II** and **1-IV** (and **1-0**), the phenyl and tropylium groups are essentially parallel; whereas, in the species that have an odd number of CH_2, the phenyl and tropylium group are inclined to each other. The parallel shape of each monomer could lead to a better packing force[25] than that of the inclined shape, resulting in different behavior for molecules that have an even and an odd number of CH_2 group (Scheme 1). This effect is similar to the odd-even effect in *n*-alkanes, where odd-numbered alkanes were found to have lower melting points than even-number alkanes.[12b]

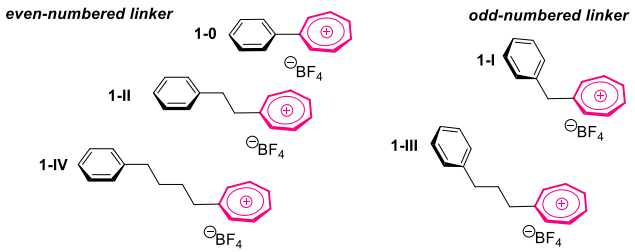


Figure 6. General shape for monomers of ω-phenyl *n*-alkyl tropylium salts **1** containing an even or odd number of CH_2.

In head-to-head dimers, the partial positive charges are close to each other, which may lead to strong electrostatic repulsions. Taking into account the presence of BF_4^- counter-ions, however, most head-to-head dimers have stronger binding free energy than head-to-tail dimers (except dimers of **1-0**). This result indicates that the interactions of other components in each dimer, i.e., BF_4^- counter ion, could play important role in the formation of unusual head-to-head π-stacking dimer via through-space electrostatic attractions as revealed by molecular electrostatic potentials (see Figure S18 in the SI).

To shed more light on the formation of unusual head-to-head dimers of compound **1-IV**, symmetry-adapted perturbation theory (SAPT)[26] is then applied using SAPT0 algorithm to dissect noncovalent interaction energy (E_{int}) into physically meaningful terms, including electrostatic (E_{elstat}), exchange repulsion (E_{exch}), polarization (E_{pol}), dispersion (E_{disp}), and charge transfer (E_{ct}).[27] Interestingly, a strong correlation ($R^2 = 0.91$) between relative interaction energies ΔE_{int} obtained from SAPT0 calculations and binding free energies ΔG_{bind} is found (Figure 7). This result gives a solid validation for our SAPT0 results.

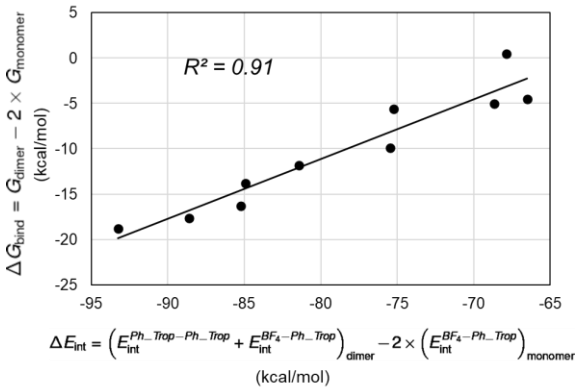


Figure 7. Correlation between relative interaction energies ΔE_{int} and binding free energies ΔG_{bind}. $E_{\text{int}}^{Ph\_trop-Ph\_trop}$ and $E_{\text{int}}^{BF_4-Ph\_Trop}$ values are phenylalkyl tropylium – phenylalkyl tropylium and BF_4^- anion – phenylalkyl tropylium interaction energies, respectively.

Energy components dissected from interaction energies of all dimers using the SAPT0 algorithm are shown in Table 2. In the interaction of phenylalkyl tropylium – phenylalkyl tropylium, because of the close distances of two partial positive charges, the electrostatic interactions are unfavored indicated by positive $E_{\text{elstat}}^{Ph\_Trop-Ph\_Trop}$ values. Whereas interactions between tropylium/phenyl – tropylium rings are mainly driven by dispersion interaction. This result is consistent with the previous study by Crittenden and coworkers suggesting that the dispersion force drives dicationic dimer formation.[19] The $E_{\text{disp}}^{Ph\_Trop-Ph\_Trop}$ interaction for head-to-tail dimers are stronger than that in head-to-head ones indicating that the ring – ring dispersion interaction is stronger in head-to-tail complexes, which is in agreement with the shorter ring – ring distances in head-to-tail dimers than that in head-to-head ones (Figure 4). In all dimers, because of the absence of bulky substituent group, Pauli repulsion terms E_{exch} are quite small compared to other components and do not play important role in the interactions of monomers.

Table 2. Energy decomposition analysis for noncovalent interactions of phenylalkyl tropylium – phenylalkyl tropylium (denoted as *Ph_Trop–Ph_Trop*) and BF_4^- anions – phenylalkyl tropyliums (denoted as *BF_4–Ph_Trop*) in all dimers. Energy values are in kcal/mol.

Dimer	ΔG_{bind}	ΔE_{int}[b]	Interaction	E_{int}[c]	E_{elstat}	E_{exch}	E_{pol}	E_{disp}	E_{ct}
1-0_HH	−17.7	−88.6	*Ph_Ttrop–Ph_Trop*	46.8	54.2	11.0	−2.1	−13.9	−0.4
			BF_4–Ph_Trop	−306.4 (−76.6)	−287.7	31.0	−35.1	−11.7	−2.9
1-0_HT[a]	−18.8	−93.3	*Ph_Ttrop–Ph_Trop*	41.5	47.9	14.1	−5.0	−14.9	−0.6
			BF_4–Ph_Trop	−303.7 (−75.9)	−285.0	31.6	−33.6	−14.0	−2.7
1-I_HH	−16.3	−85.2	*Ph_Ttrop–Ph_Trop*	47.2	50.3	0.0	−1.6	−1.5	0.0
			BF_4–Ph_Trop	−308.1 (−77.0)	−291.0	31.8	−33.4	−13.6	−2.0
1-I_HT	−4.5	−66.5	*Ph_Ttrop–Ph_Trop*	36.6	41.1	5.4	−1.6	−8.2	−0.2
			BF_4–Ph_Trop	−278.9 (−69.7)	−261.3	29.8	−32.8	−12.3	−2.3
1-II_HH	−13.8	−84.9	*Ph_Ttrop–Ph_Trop*	51.8	58.6	4.8	−3.2	−8.2	−0.2
			BF_4–Ph_Trop	−308.1 (−77.0)	−286.6	29.2	−36.5	−11.6	−2.6
1-II_HT[a]	−9.9	−75.5	*Ph_Ttrop–Ph_Trop*	36.1	39.0	13.1	−3.3	−12.4	−0.3
			BF_4–Ph_Trop	−283.0 (−70.7)	−262.2	27.2	−34.1	−11.5	−2.3
1-III_HH	−5.6	−75.2	*Ph_Ttrop–Ph_Trop*	52.3	58.5	5.2	−2.7	−8.5	−0.2
			BF_4–Ph_Trop	−304.0 (−76.0)	−281.5	30.5	−37.7	−12.3	−2.9
1-III_HT	0.4	−67.9	*Ph_Ttrop–Ph_Trop*	30.5	33.5	12.4	−3.4	−11.6	−0.4
			BF_4–Ph_Trop	−274.8 (−68.7)	−253.2	28.7	−35.5	−12.4	−2.5
1-IV_HH[a]	−11.8	−81.4	*Ph_Ttrop–Ph_Trop*	52.5	58.7	5.9	−2.8	−9.1	−0.2
			BF_4–Ph_Trop	−306.6 (−76.7)	−283.5	28.8	−37.2	−11.9	−2.9
1-IV_HT	−5.0	−68.7	*Ph_Ttrop–Ph_Trop*	28.5	31.4	12.4	−2.9	−12.1	−0.3
			BF_4–Ph_Trop	−269.9 (−67.5)	−245.4	25.2	−35.5	−11.9	−2.2

[a] Dimers that are found in the corresponding crystal structures.

[b] Relative interaction energy is calculated as $\Delta E_{\text{int}} = \left(E_{\text{int}}^{Ph\_Trop-Ph\_Trop} + E_{\text{int}}^{BF_4-Ph\_Trop}\right)_{\text{dimer}} - 2 \times \left(E_{\text{int}}^{BF_4-Ph\_Trop}\right)_{\text{monomer}}$. $E_{\text{int}}^{BF_4-Ph\_Trop}$ is the summation of four pair-wise interactions between BF_4^- anion and phenylalkyl tropylium in a dimer.

[c] The number in parenthesis is the average value for one BF_4–Ph_Trop interaction in a dimer.

Importantly, in all dimers, strong electrostatic interactions between BF_4^- anions and phenylalkyl tropyliums are found, which compensates phenylalkyl tropylium – phenylalkyl tropylium electrostatic repulsion $E_{\text{elstat}}^{Ph\_Trop-Ph\_Trop}$ and dominants all interactions. It should be notice that only one BF_4–Ph_Trop interaction is sufficient to balance the Ph_Ttrop–Ph_Trop repulsion, which indicates that other three BF_4–Ph_Trop interactions can be employed to stabilize the structure rendering stable dimer complexes. The $E_{\text{elstat}}^{BF_4-Ph\_Trop}$ values in head-to-head dimers are found to be stronger than that in head-to-tail complexes resulting in the more favorable formation of head-to-head dimers (except dimers of **1-0**). These findings suggest that through-space electrostatic interactions are the main origin for the complexation of all dimers, in particular for head-to-head dimers, leading to the head-to-head arrangement in phenylalkyl tropylium salt **1-IV** in crystalline environment. In the **1-0_HH** and **1-0_HT** dimers, because the distances between tropylium groups and BF_4 cations are similar, the $E_{\text{elstat}}^{BF_4-Ph\_Trop}$ values are comparable. The dimer formation of **1-0** is therefore driven by the phenylalkyl tropylium – phenylalkyl tropylium interactions. Because of the weaker electrostatic repulsion and stronger dispersion attraction, the head-to-tail arrangement of **1-0** is more favorable.

CONCLUSION

In brief, we have developed a series of novel ω-phenyl *n*-alkyl tropylium tetrafluoroborates with interesting alternation in their physical and photophysical characters. The odd-numbered linker compounds are novel room-temperature ionic liquids while the even-numbered linker analogues are clusteroluminogenic molecules. The curious photoluminescent properties of these compounds can be attributed to their ability to form unusual through-space charge-transfer complexes to trigger crystallization-induced emission enhancement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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