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## COMMUNICATION

## Multi-colour and red emissions from a small donor-acceptor molecule by breaching Kasha's rule

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Reported herein is a small (MW 260 Da) organic molecule that emits multicolour and red lights, capitalising simultaneous anti-Kasha and donor-acceptor effects. The molecule emits from two excited states, namely  $S_1$  and  $S_3$ . Introduction of donor-acceptor substituents resulted in the large Stokes shifts ( $>5000\text{ cm}^{-1}$ ) with negligible spectral overlap.

Multi-colour organic emitters are of great importance in real-life applications including multi-colour bioimaging, multi-colour display technologies, white light emissions, anti-counterfeiting, etc.<sup>1</sup> In particular, small organic fluorophores are highly desirable because of their improved cell permeability, reduced perturbation of biological function, and simplicity in solid-state device fabrication.<sup>2</sup> However, achieving broad colour tunability from blue to red within a single, low-molecular-weight molecule remains a formidable challenge. Most red-emissive organic systems rely on extensive  $\pi$ -conjugation or multiple donor-acceptor substitutions, frequently leading to high molecular weights (often  $\geq 300\text{ Da}$ ), diminished quantum yields, and predominantly single-colour emission.<sup>3</sup> Herein we describe a small organic molecule with a molecular weight of 260 Da that (i) emits red light in both solid and solution; (ii) produces multiple colours as a function of excitation wavelengths by breaching Kasha's rule and (iii) displays large Stokes shifts with little spectral overlap between absorption and emission bands. Such multifaceted properties from a single yet small molecule are unique and represent a noteworthy advance in molecular photophysics.

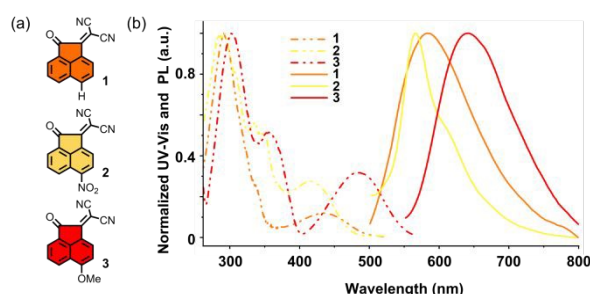


Figure 1. (a) Chemical structure of compounds **1–3** and (b) Normalized absorption (dotted line) and PL (solid line,  $\lambda_{\text{ex}} = \lambda_{\text{max}}$ , Table 1) in ACN at  $10^{-5}\text{ M}$ .

The design of this molecule stemmed from two basic concepts: first, the presence of an acenaphthylene core, which exhibits anti-Kasha emission<sup>4</sup> and second, the strategic installation of donor-acceptor substituents on opposite sides of the acenaphthylene core to obtain red-shifted emission<sup>5</sup> and large Stokes shifts,<sup>6</sup> which would lead to poor overlap between absorption and emission bands.<sup>7</sup> Furthermore, realising anti-Kasha emissions from a donor- $\pi$ -acceptor (D- $\pi$ -A) architecture is particularly appealing, as such systems hold promise for advanced applications, including ratiometric bioimaging, detection of cellular microenvironments, photodynamic therapy, etc.<sup>8</sup>

Recently, we reported vicinal diones like, acenaphthylene-1,2-dione, phenanthrene-9,10-dione, and pyrene-4,5-dione and their derivatives that can disobey Kasha's rule and emit from multiple excited states,<sup>9</sup> leading to multi-colour and even white light emissions.<sup>10</sup> However, these emissions were largely confined to the green–yellow region ( $\sim 550\text{ nm}$ ). To extend the emission into the red region, we designed compound **3** comprising an electron donor substituent (OMe) at one end of the acenaphthylene-1,2-dione and to make the other side a better acceptor, one of the carbonyl groups was reacted with malononitrile (Figure 1a). For comparison, analogues bearing an electron-withdrawing nitro group (**2**) and no substituent (**1**)

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## COMMUNICATION

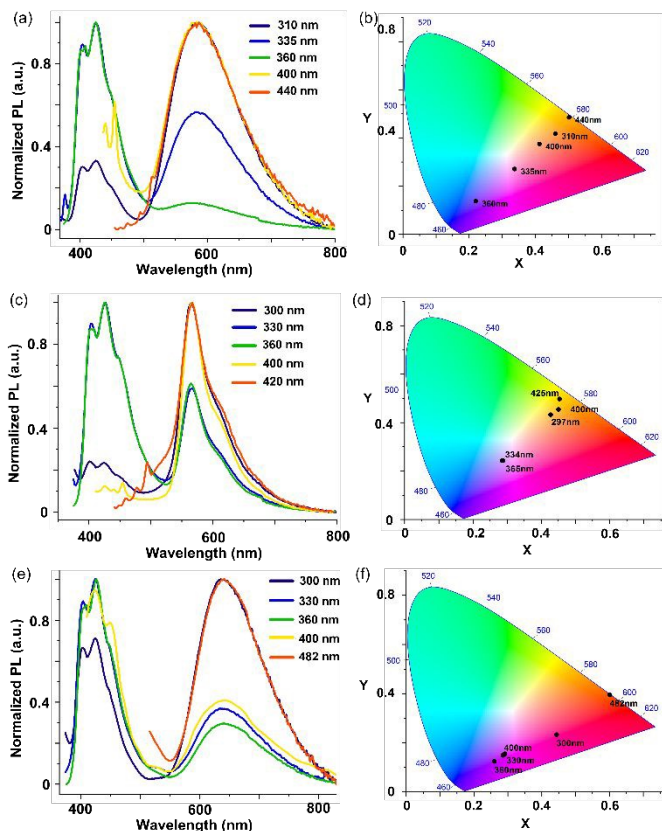
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Figure 2. Excitation wavelength-dependent emission studies of compounds (a) **1**, (b) **2** and (c) **3** and their corresponding CIE plots (d) **1**, (e) **2** and (f) **3** in ACN at  $10^{-5}$  M.

were also synthesised. These molecules display two emission bands, one in the blue region and another in the yellow to red (based on the substituents). The effect of substituents is clearly visible in their longer wavelength emissions; compound **3** emits in the most red-shifted region, while that of **2** in the most blue-shifted region. Compound **1** exhibited emission that fell in between **2** and **3**. Interestingly, the high-energy emission bands did not display any substituents effects, implying that the emission may solely originate from the acenaphthylene core. This clear separation of emissive underpins the excitation-dependent multicolour behaviour observed in these compact molecules.

The synthesis of these derivatives and characterisation are presented in the supporting information, and the purity was confirmed using high-performance liquid chromatography (HPLC) (ESI†, Figure S1-10) and elemental analysis.<sup>11</sup> Single crystal structures of compounds **1** and **3**, and HRMS further confirm the integrity of these molecules (ESI†, Figure S32-33). Their absorption spectra revealed that compounds **1–3** possess three absorption bands (Figure 1b). While compound **3** absorbs

in the most red-shifted region ( $\lambda_{ab} = 482$  nm), compound **2** exhibited the most blue-shifted absorption bands ( $\lambda_{ab} = 414$  nm), and the same for **1** appeared to be in between ( $\lambda_{ab} = 435$  nm), clearly indicating a strong substituents effect. Interestingly, all the compounds showed minimal solvatochromism in solvents of different polarities (Figure S17-S19); the absorption maxima slightly red-shifted for compounds **1** and **3**, indicating that the excited state is more polar compared to the ground state. This, however, is not true for **2**; the absorption band at 414 nm undergoes hypsochromic shifts, implying that the ground state is more polar compared to the excited state.<sup>12</sup> Next, we recorded their emission spectra in acetonitrile ( $c = 10^{-5}$  M, Figure 1b, Table 1). Excitation ( $\lambda_{ex} = 435$  nm) of **1** resulted in an emission band at 587 nm ( $\phi_{PL} = 5.56 \pm 0.31\%$ ,  $\tau_{PL} = 5.37 \pm 0.10$  ns). However, for **2** ( $\lambda_{ex} = 414$  nm), the emission band shifted towards blue and appeared at 567 nm ( $\phi_{PL} = 1.14 \pm 0.29\%$ ,  $\tau_{PL} = 1.67 \pm 0.04$  ns). As expected, **3** exhibited the most red-shifted emission band at 642 nm ( $\phi_{PL} = 2.84 \pm 0.39\%$ ,  $\tau_{PL} = 1.41 \pm 0.12$  ns,  $\lambda_{ex} = 482$  nm).<sup>13</sup> These data indicate the effect of the donor-acceptor system in a small molecule to shift the emission wavelength into the red region. Interestingly, all three molecules exhibit large Stokes shifts of over  $5000$   $\text{cm}^{-1}$  with the largest value of  $6520$   $\text{cm}^{-1}$  for compound **2**, resulting in a negligible spectral overlap (ESI† Table S1).

As the molecules exhibit multiple absorption bands, we decided to excite them at different wavelengths to investigate their possible anti-Kasha effects. Excitation ( $\lambda_{ex} = 310$  nm) of **1** resulted in a strong emission band at 425 nm along with a band at 587 nm (Figure 2a, d). However, the latter became the sole emission band at  $\lambda_{ex} = 440$  nm. This resulted in the emission colours that ranging from blue to yellow. Similarly, compound **2** exhibited two emission bands at 425 nm and 567 nm when the excitation wavelengths were tuned: yielding colours that changing from blue to orangish-yellow (Figure 2b, e). Not surprisingly, compound **3** was found to display excitation wavelength-dependent emissions; the shorter wavelength emission was observed at 426 nm while the longer wavelength emission was at 642 nm, illuminating colours from blue to red

Table 1. Photophysical properties of compounds **1–3** in solution.

Compound <sup>a</sup>	$\lambda_{abs}$ (nm) <sup>b</sup>	$\lambda_{em}$ (nm) <sup>c</sup>	$\tau_{FL}$ (ns) <sup>d</sup>	$\Phi_{FL}$ (%) <sup>e</sup>	$\lambda_{em}$ (nm) <sup>f</sup>	$\tau_{FL}$ (ns) <sup>g</sup>	$\Phi_{FL}$ (%) <sup>h</sup>
<b>1</b>	435	425	$1.61 \pm 0.01$	$7.45 \pm 0.21$	587	$5.37 \pm 0.10$	$5.56 \pm 0.31$
<b>2</b>	414	425	$1.27 \pm 0.23$	$2.64 \pm 0.39$	567	$1.67 \pm 0.04$	$1.14 \pm 0.29$
<b>3</b>	482	426	$1.57 \pm 0.03$	$5.15 \pm 0.19$	642	$1.41 \pm 0.12$	$2.84 \pm 0.30$

<sup>a</sup> Photophysical studies were measured in ACN at  $c = 10^{-5}$  M. <sup>b</sup> Absorption maxima of all three compounds. <sup>c</sup> Emission data recorded for all three compounds at  $\lambda_{ex} = 360$  nm. <sup>d</sup> Lifetimes ( $\lambda_{ex} = 340$  nm) and relative PLQYs of compounds **1–3** for high energy emission bands. <sup>e</sup> Emission maxima recorded at  $\lambda_{ex(1)} = 435$  nm,  $\lambda_{ex(2)} = 414$  nm and  $\lambda_{ex(3)} = 482$  nm. <sup>f</sup> Lifetimes ( $\lambda_{ex} = 450$  nm) and relative PLQYs of compounds **1–3** for low energy emission bands.

(Figure 2c, f). These data clearly indicated that the high energy emission is independent of substituents ( $\Delta\lambda_{em} = 1$  nm) and



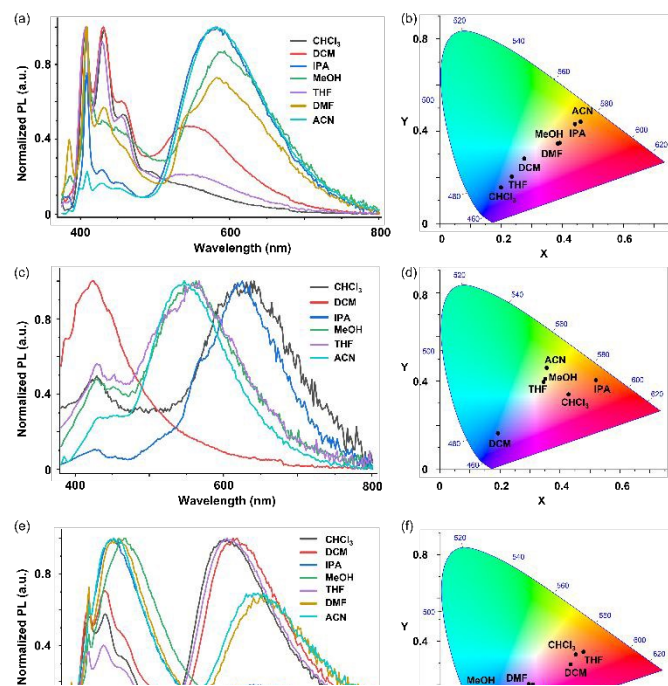


Figure 3. Emission studies of compounds **1-3** in solvents of different polarities. (a), (c) and (e) are normalized emission spectra, and (b), (d) and (f) are the corresponding CIE plots of **1**, **2** and **3**, respectively.  $\lambda_{\text{ex}} = 365$  nm for all compounds.

primarily involved core-to-core electronic transition, while the red-shifted emission band is highly substituent dependent ( $\Delta\lambda_{\text{em}} = 75$  nm). The excitation spectra recorded for each of these emission bands clearly indicated that compounds **1-3** may emit from multiple excited states by breaching Kasha's rule (ESI<sup>†</sup>, Figure S12-14). Furthermore, the lifetimes and quantum yields for these emission bands are different, confirming that they originated from different excited states (Table 1, ESI<sup>†</sup>, Figure S23-25). To further prove that the two emission bands were not originating from impurities, 2D excitation-emission correlation diagrams were plotted for all the compounds. A strong correlation between the emission bands indeed supports that the emissions originate from the same compounds (ESI<sup>†</sup>, Figure S12-14).<sup>14</sup>

Interestingly, all three molecules exhibited strong solvatochromism, resulting in a dramatic change in their emission behaviour (Figure 3, ESI<sup>†</sup>, Figure S17-19). For example, for compound **1**, the  $\lambda_{\text{em}} = 425$  nm band did not show any shifts but changed its intensity upon changing the polarity (Figure 3a, b). On the contrary, the red-shifted emission band ( $\lambda_{\text{em}} = 587$  nm) showed significant shifts and increased in intensity, indicating a strong charge-transfer character and the stabilisation of the excited state in polar solvents, which is in accordance with the absorption studies. Consequently, a wide range of colour tunability from blue to orangish-yellow, including near-white light (DCM, CIE coordinates 0.27, 0.28) was observed (ESI<sup>†</sup>, Figure S17). By contrast, for compound **3**, the intensity of the  $\lambda_{\text{em}} = 642$  nm band dramatically reduced accompanied by the red shifts in more polar solvents (Figure 3e, f). This could be due to the stabilization of the excited state along with the opening of a non-radiative channel, possibly by the rotation of the methoxy group.<sup>15</sup> Nevertheless, it showed a nice colour tunability in various solvents from blue to orange

(ESI<sup>†</sup>, Figure S19). Solvatochromism was also demonstrated by compound **2**. As the solvent polarity increased, the emission peak at 567 nm shifted towards blue, suggesting that the ground state is more polar and stabilised by the polar solvents (Figure 3c, d). It is unclear, nevertheless, why the emission intensity significantly decreased at  $\lambda_{\text{em}} = 425$  nm. Overall, all three derivatives exhibited a charge transfer character of their low energy emission band, and for compounds **1** and **3** the excited state is more polar, while for **2**, it is the ground state.

Finally, the solid-state emissions of these new molecules were recorded. Interestingly, the changing of excitation energy did not result in the multiple emission bands, a common feature of molecules that obey Kasha's rule. This can be explained from the crystal structure of compounds **1** and **3** (Figure 4a). The very short intermolecular distance, through  $\pi$ - $\pi$  stacking, speeds up the rate of IC from the higher excited state(s), yielding emission only from the lowest excited state (i.e.  $S_1$ ). Nevertheless, compounds **1** and **3** exhibited significant red shifts (595 nm and 673 nm, respectively) in their solid state compared to solution state emission (Figure 4b). On the contrary, compound **2** displayed blue shifts (535 nm) in its solid-state emission. Although the aggregation-induced emission<sup>16</sup> (i.e. in the solid state) often resulted in bathochromic shifts, the hypsochromic shifts for **2** can be possibly attributed to the smaller reorganisation energy in the solid state compared to its solution state.<sup>17</sup> Nevertheless, **3** yielded red light in its solid state.<sup>18</sup>

To understand the photophysical behaviour of these compounds, we performed geometry optimisation and calculated their absorption and emission spectra using PBE functional and 6-311+g(d,p) basis set.<sup>19</sup> The highest occupied molecular orbitals (HOMO) of all compounds reside on the aromatic core and partly on the substituents, while that of the lowest unoccupied molecular orbitals (LUMO) is on the carbonyl and malononitrile segments, which are largely separated, and thus, indicates a charge transfer nature of electronic transitions between the HOMO and LUMO (Figure 4d, ESI<sup>†</sup>, Figure S34). The calculated absorption spectra revealed that the electronic transitions occurred from  $S_0$  to  $S_1$ ,  $S_3$ ,  $S_4$  and  $S_5$  ( $S_2$  is a dark state), resulting in the multiple bands in the electronic absorption spectra. However, the emission spectra, on the other hand, showed two relaxation processes,  $S_3 \rightarrow S_0$  (blue-shifted band) and  $S_1 \rightarrow S_0$  (red-shifted band), which involve HOMO-1  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO electronic transitions, respectively (ESI<sup>†</sup> Table S8-S13). As depicted in figure 4d, all the transitions are  $\pi^* \rightarrow \pi$  types. Furthermore, although the substituents' contribution to the HOMO orbitals is noticeable in all compounds, the HOMO-1 orbitals lack it entirely. Consequently, there will be strong substituent effects in the low-energy emission band. On the other hand, the high-energy emission band may not exhibit a substituent effect, consistent with the experimental results. Additionally, the dipole moments in the ground state of the optimised structures are relatively high for compounds **1** and **3** (11.13 D and 12.94 D, respectively), and they are increased in the first excited state to 12.41 D and 15.09 D, respectively. On the contrary, the dipole moment in the ground state of **2** is low (only 5.61 D), while the same is marginally reduced to 5.17 in the first excited state. These data



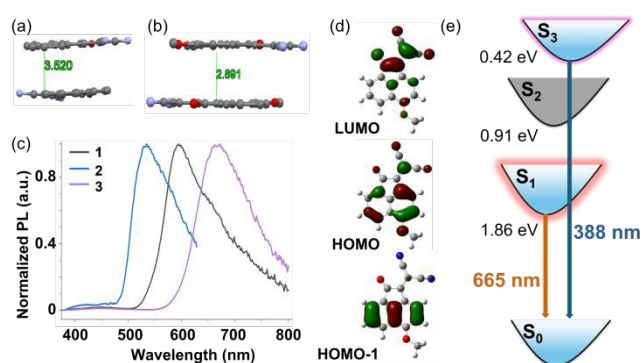


Figure 4. Solid state packing of compounds (a) **1** and (b) **3** displaying their intermolecular distances. (c) Solid state fluorescence spectra of compounds **1-3** ( $\lambda_{\text{ex}} = 365$  nm). (d) Calculated natural transition orbitals (NTOs) of compounds **3** using PBE functional and 6-311+g(d,p) basis set for  $S_0 \rightarrow S_1$  absorption and (e) Calculated emissive states of compound **3**. The energy levels are reported from the optimised  $S_1$  state.

also support the experimental data, suggesting that the first excited state is more polar for **1** and **3** and possesses strong charge transfer character, while the ground state is more polar for **2** and may not display significant charge transfer character. The calculated emission spectra of **3** revealed that the  $S_1$  and  $S_3$  are the bright state that emit in the visible range (Figure 4e). The energy differences between  $S_1$  and  $S_2$  and  $S_2$  and  $S_3$  are 0.91 eV and 0.42 eV, respectively. Fluorescence from higher excited states is made possible by a relatively large  $\Delta E_{S_3-S_2}$ , which essentially lowers the rate of IC. Remarkably,  $S_2$  was found to be a dark state with a zero oscillator strength. This makes us believe that the blue-shifted emission possibly occurs from  $S_3$ , which perfectly matches with that of the experimental data ( $\lambda_{\text{em(calc.)}} = 388$  nm,  $\lambda_{\text{em(expt.)}} = 426$  nm). This is also true for the low energy emission band ( $\lambda_{\text{em(calc.)}} = 665$  nm,  $\lambda_{\text{em(expt.)}} = 642$  nm) that originates from  $S_1$  (Figure 4e). The calculated emission spectra also agreed well for the compounds **1** and **2**. Thus, it is evident from both experimental and theoretical data that the malononitrile-substituted acenaphthylene diones violate Kasha's rule by emitting from two distinct excited states.

In summary, we report three donor-acceptor small organic molecules that emit in the red region with large Stokes shifts yet without affecting the anti-Kasha emissions of the core acenaphthylene moiety. TDDFT calculations support the presence of two bright states, namely  $S_1$  and  $S_3$ , while  $S_2$  remains a dark state, resulting in a nice colour tunability from blue to red as a function of excitation wavelength. Additionally, the introduction of donor-acceptor substituents yielded red-emitting species in both solution and the solid state, particularly for compound **3**, as evidenced by the molecular orbital distribution on the acenaphthylene core. Consequently, this study will pave the way towards the development of multi-coloured and red emissive small molecules that can be useful in various fields, including the fabrication of multi-colour OLEDs, anticounterfeiting, bioimaging and photodynamic therapy.<sup>20</sup>

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## Data availability

The data supporting this paper have been included as part of the SI. Supplementary information: Detailed synthetic procedure, characterization, necessary spectra, and theoretical data.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

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## Data availability

The data supporting this paper have been included as part of the SI. Supplementary information: Detailed synthetic procedure, characterization, necessary spectra, and theoretical data.

