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We report the synthesis, X-ray structure and photophysical properties of a few benzoylpyrene (BP) derivatives. Steric hindrance due to incremental benzoyl groups causes a systematic reduction in the orbital overlap (π – π) between vicinal pyrene units affording green-yellow-orange solid-state emitters. Crystallization induced emission could arise from i) electronic (dipolar/excitionic) interactions; ii) arrested bond rotations and/or iii) lack of solvation in the crystalline (Φ_{FI} ~2–26%) 1-4BP when compared to that in solution (Φ_{FI} ≤1%). Our effort [*Chem. Commun.* 2014, *50*, 8644] on progressive acylation, in contrast to benzoylation, results in gradual increase in the π – π overlap between vicinal pyrenes.

1. Introduction

Pyrene is considered as fruit fly of photochemists by virtue of its fundamental and applied research interests.¹ Since the discovery of pyrene in 1837,² this unique chromophore is well-exploited for diverse applications in biology and material science owing to its inherent photochemical stability. Crystalline pyrene based blue organic light emitting devices (OLED) suffer from strong excimer contributions.³ Disruption of nearest neighbour interactions in crystalline pyrene is expected to enhance the performance of OLEDs.⁴ A variety of chemical⁵ and physical approaches⁶ have been utilized to regulate the pyrene-pyrene interactions. Physical methods to tune these interactions⁷ involve mechanical grinding,⁸ sublimation⁹ or solvent-/co-crystallization.^{6a} Chemical methods¹⁰ employ steric effects imparted by bulky groups that can be conveniently functionalized through electrophilic substitution reactions. Most of such attempts led to the conversion of dimeric to monomeric pyrene, resulting in a shift from "deep-blue" to "sky-blue" solid state emission.¹¹ Yet the synthesis and structure-property correlation of pyrene based non-blue solid state emitters has received less attention.

Recently, we utilised interchromophoric interactions of pyrene to understand the distribution of parallel vs. antiparallel G-quadrulex conformations in aqueous and non-aqueous media.¹² Efforts to tune the interchromophoric interactions in molecular crystals using $\pi - \pi$,¹³ C-H••• π ,¹⁴ C-H•••O¹⁵ and C-H•••H-C¹⁶ contacts for favourable photophysical properties facilitated us to employ the combination of steric and conjugation effects of benzoyl units

of pyrene based system. In our earlier effort,^{13a} progressive acylation of pyrene resulted in remarkable decrease in the interplanar angle between two neighbouring units causing significant red-shift in the solid-state fluorescence. Significant dimension of benzoyl unit (129.4 Å³)¹⁷ as compared to pyrene (237.5 Å³) could potentially perturb strong π - π interactions (-13.8 kcal/mol)¹⁸ between the nearest pyrene units (center-to-center distance of 3.53 Å; Fig. S1; ESI⁺). In addition, conjugation arising from incremental benzoyl units progressively influences the HOMO-LUMO gap that could result in the bathochromic shift in electronic absorption and



Scheme 1. Row I: Molecular structure of 1–4BP; Row II: close packing arrangement in the crystal a) 1BP; b) 2BP; c) 2'BP; d) 2''BP; e) 3BP and f) 4BP; Row III: photographic image of the crystals in daylight (above) and under UV illumination (below).

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emission properties. We herein report simple Friedel-Crafts benzoylation of pyrene (Scheme 1, row I) that results in the formation of green-yellow-orange luminescent crystals. In contrast to acylation of pyrene,^{13a} progressive benzoylation of pyrene resulted in significant decrease in the π - π interactions causing systematic blue-shift in the emitted light in the crystalline state. Crystallization induced emission (CIE) possessing precise emission colour tunability in benzoylpyrene derivatives indicates the possibility for novel light emitting devices.

2. Experimental

2.1 Materials and methods

Reactions were carried out in oven-dried glassware prior to use and wherever necessary, were performed under dry nitrogen in dried, anhydrous solvents using standard gastight syringes, cannulae, and septa. Solvents were dried and distilled by standard procedures. Flash column chromatography was performed using silica gel of 200-400 mesh employing a solvent polarity correlated with the TLC mobility observed for the substance of interest. Yields refer to chromatographically spectroscopically homogenous and substances. High Resolution Mass Spectra (HRMS) were recorded on Agilent 6538 Ultra High Definition (UHD) Accurate-Mass Q-TOF-LC/MS system using either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) mode. ¹H and ¹³C NMR spectra were measured on a 500 MHz Bruker advanced DPX spectrometer. Internal standard used for ¹H and ¹³C NMR is 1,1,1,1-tetramethyl silane (TMS). All the elemental analyses were performed on Elementar Vario MICRO Cube analyzer. All values recorded in elemental analyses are given in percentages. Reference standard used for elemental analysis is 4-aminobenzenesulphonic acid (sulphanilic acid).

2.2 Synthetic procedure

Preparation of benzoylpyrene (1-4BP) derivatives:¹⁹ Pyrene (10 g; 0.049 mols) dissolved in CS₂ (yellow solution, 250 mL) was maintained at ambient temperature and subsequently anhydrous AlCl₃ was added. Benzoyl chloride (27.80 g; 0.198 mols) was then slowly syringed to the suspension. Subsequently, hydrogen chloride was liberated. After 3 hrs the mixture was added slowly to a vigorously stirred mixture of ice and concentrated HCl. The resulting suspension was filtered vacuum dried and purified through column and chromatography (silica gel) to give benzoylpyrene (1-4BP) derivatives.

1BP (yield= 5.1%) M.p. 102-105 °C. ¹H NMR [500 MHz, DMSO(d₆), δ]: 8.40 (m, 4H), 8.43 (q, J = 9.66 Hz, 2H), 8.17 (m, 3H), 7.82 (d, J = 7.7 Hz, 2H), 7.73 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 7.8 Hz, 2H). ¹³C NMR [125 MHz, DMSO(d₆), δ]: 197.56, 138.0, 133.60, 132.82, 132.46, 130.70, 130.08, 129.07, 128.90, 128.83, 128.66, 127.25, 126.83, 126.68, 126.35, 126.04, 124.20, 124.10, 123.84, 123.55. IR (KBr, cm⁻¹): 3037, 1651, 1595, 1506, 1446. Elemental analysis: calcd. value for C₂₃H₁₄O:

90.17% C, 4.61% H; found: 90.31% C, 4.56% H. HRMS (ESI) m/z calculated for $C_{23}H_{14}O$ [M]⁺: 306.1045, found: 306.1037.

2BP (yield= 9.4%) M.p. 164-167 °C. ¹H NMR [500 MHz, DMSO(d₆), δ]: 8.50 (d, *J* = 7.7, 2H), 8.43 (d, *J* = 9.3 Hz, 2H), 8.32 (d, *J* =9.2 Hz, 2H), 8.25 (t, *J* = 7.7 Hz, 1H), 8.13 (s, 1H), 7.88 (d, *J* = 8.2, 4H), 7.71 (t, *J* = 7.5, 2H), 7.57 (t, *J* = 7.8, 4H). ¹³C NMR [125 MHz, DMSO(d₆), δ]: 201.94, 131.41, 131.21, 130.37, 129.87, 128.03, 127.43, 127.20, 124.39, 124.18, 123.19, 30.71. IR (KBr, cm⁻¹): 3053, 1656, 1585, 1516, 1446. Elemental analysis: calcd. value for $C_{30}H_{18}O_2$: 87.78% C, 4.42% H; found: 87.63% C, 4.61% H. HRMS (ESI) m/z calculated for $C_{30}H_{18}O_2$ [M]⁺: 410.1307, found: 410.1305.

2'BP (yield= 9.6%) M.p 233-238 °C. ¹H NMR [500 MHz, DMSO(d₆), δ]: 8.38 (d, *J* = 8 Hz, 2H), 8.25 (d, *J* = 9.5 Hz, 2H), 8.18 (d, *J* = 9.5 Hz, 2H), 8.10 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 4 H), 7.64 (t, *J* = 7.1, 2H), 7.49 (t, *J* = 7.7, 4H). ¹³C NMR [125 MHz, DMSO(d₆), δ]: 202.20, 133.33, 132.31, 129.07, 128.20, 127.73, 126.39, 125.35, 123.73, 30.64. IR (KBr, cm⁻¹): 3051, 1649, 1571, 1490, 1442. Elemental analysis: calcd. value for C₃₀H₁₈O₂: 87.78% C, 4.42% H; found: 87.71% C, 4.69% H. HRMS (ESI) m/z calculated for C₃₀H₁₈O₂ [M]⁺: 410.1307, found: 410.1301.

2"BP (yield= 37.5%) M.p. 155-158 °C. ¹H NMR [500 MHz, DMSO(d₆), δ]: 8.42 (d, *J* = 7.5 Hz, 2H), 8.35 (s, 2H), 8.11= (d, *J* = 3 Hz, 2H), 8.09 (s, 2H), 7.71 (d, *J* = 8.25, 4H), 7.61 (t, *J* = 8.5, 2H), 7.47 (t, *J* = 7.25, 4H). ¹³C NMR [125 MHz, DMSO(d₆), δ]: 197.82, 138.27, 134.29, 134.25, 132.99, 130.63, 129.43, 129.36, 128.57, 127.54, 126.14, 125.97, 126.14, 124.22. IR (KBr, cm⁻¹) 3051, 1654, 1595, 1446, 1446. Elemental analysis: calcd. value for $C_{30}H_{18}O_2$: 87.78% C, 4.42% H; found: 87.68% C, 4.59% H. HRMS (ESI) m/z calculated for $C_{30}H_{18}O_2$ [M]⁺: 410.1307, found: 410.1298.

3BP (yield= 18.9%) M.p. 183-187 °C. ¹H NMR [500 MHz, DMSO(d₆), δ]: 8.63 (d, J = 9.7 Hz, 1H), 8.54 (d, J = 9.3 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.35 (s, 2H), 8.30 (d, J = 7.8 Hz, 1H), 8.23 (s, 1H), 8.89 (m, 4H), 7.85 (d, J = 7.7 Hz, 2H), 7.75 (m, 3H), 7.63 (m, 6H). ¹³C NMR [125 MHz, DMSO(d₆), δ]:197.18, 196.63, 196.52, 137.60, 137.48, 137.43, 135, 133.93, 133.90, 132.89, 132.65, 131.81, 130.42, 130.27, 130.26, 130.17, 129.77, 128.90, 128.88, 128.85, 128.06, 127.34, 127.22, 127.17, 126.44, 125.50, 124.50, 124.15, 123.64. IR (KBr, cm⁻¹): 3055, 1654, 1593, 1568, 1446. Elemental analysis: calcd. value for C₃₇H₂₂O₃: 86.36% C, 4.31% H; found: 87.41% C, 4.45% H. HRMS (ESI) m/z calculated for C₃₇H₂₂O₃ [M]⁺: 514.1569, found: 516.1552.

4BP (yield= 1.9%) M.p. 283-285 °C. ¹H NMR [500 MHz, DMSO(d₆), δ]: 8.33 (s, 4H), 8.20 (s, 2H), 7.81 (d, *J* = 9.25 Hz, 8H), 7.65 (t, *J* = 7.85 Hz, 4H), 7.50 (t, *J* = 7.85 Hz, 8H). ¹³C NMR [125MHz, DMSO(d₆), δ]:196.93, 137.82, 134.56, 134.39, 130.80, 130.19, 129.41, 127.75, 127.46, 124.62. IR (KBr, cm⁻¹): 3055, 1654, 1593, 1568, 1446. Elemental analysis: calcd. value for C₄₄H₂₆O₄: 85.42% C, 4.24% H; found: 85.63% C, 4.31% H. HRMS (ESI) m/z calculated for C₄₄H₂₆O₄ [M]⁺: 618.1831 found: 618.1820.

3. Results and discussion

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Adding stoichiometric quantity of benzoyl chloride to a solution of pyrene (P) and AlCl₃ in carbon disulfide (CS₂) at ambient temperature rendered the benzoyl derivatives (1–4BP) in low-moderate yields (Scheme S1; ESI⁺). Though Harvey and co-workers¹⁹ reported 1BP, 2BP and 2'BP, the synthesis of 2"BP, 3BP and 4BP are yet to be explored. Single crystal X-ray analyses (SCXRD) of 1–4BP were not reported earlier. SCXRD analyses were performed on 0.20 x 0.20 x 0.15 mm crystalline samples obtained through slow evaporation of 1–4BP from a varying composition of chloroform:acetone mixtures (Table S1; ESI⁺). Benzoyl derivatives 1BP (*P*-1), 2BP (*P*-1) and 3BP (*P*-1) yield solvent free triclinic crystal system while 2'BP (*P*2₁/n), 2"BP (*C*2/*c*) and 4BP (*P*2₁/n) exhibit solvent free monoclinic crystal system (Scheme 1, row III, Table S2; ESI⁺).

Frontier molecular orbital (FMO) analysis, cvclic voltammetric, UV-Vis absorption and emission measurements were employed to investigate the extent of perturbations in pyrene imparted by incremental benzoyl groups. FMO analyses of 1-4BP shows that the electron density of HOMO (Fig. 1a) is distributed in pyrene units while electron density of LUMO is mostly localized on pyrene chromophore with a moderate extension to the carbonyl group(s). Low-lying excited electronic states mainly results from well-described $\pi-\pi^*$ transitions with a minor contribution from $n-\pi^*$ character. A decrease in the HOMO-LUMO gap from 3.59 eV (1BP) to 3.18eV (4BP) is attributed to the increase in the effective conjugation due to carbonyl groups on the pyrene unit (Table S3, ESI⁺). Cyclic voltammetry (0.1 M nBu₄NPF₆ in acetonitrile) of 1BP (Fig. 1b) exhibits oxidation peak at 1.47 V while reduction peak appear at -1.50 V. Decrease in the HOMO-LUMO gap of benzoylpyrenes (2.97 eV for 1BP; 2.61 eV for 4BP; Table S3; ESI⁺) in comparison to P (3.37 eV) is in agreement with the FMO analysis.²⁰

Steady state absorption spectra of 1-4BP in chloroform exhibit two distinct bands: a band centered around 250-300 nm and another around 300-425 nm (Fig. 1c). Time-dependent density functional theory (TDDFT)²¹ calculations suggest that observed bands are a combination of several electronic transitions (Table S4; ESI⁺) with the longer wavelength band due to $\pi - \pi^*$ transition. λ_{max} of long-wavelength transition of 1BP in chloroform is red-shifted by 12 nm compared to P. 2-4BP display remarkable red-shift in the long-wavelength, which could be attributed to the increase in number of benzoyl group(s). Upon excitation at 380 nm, 1BP in chloroform exhibits emission band centered around 450 nm (Fig. S2a, Table S5; ESI⁺). The emission maximum is ca. 50 nm redshifted in comparison to P under similar conditions. However, further increase in the number of benzoyl groups, the emission maximum remains unchanged (ca. 450 nm). Very low fluorescence quantum yield was observed for 1-4BP ($\Phi_{\rm Fl} \leq$ 1.0%, Table S5; ESI⁺) in chloroform when compared to P $(\Phi_{\rm Fl} = 65\%).^{22}$

Picosecond time-resolved fluorescence measurements of 1–4BP indicate very short lifetime (<100 ps pulse width at λ_{ex} =375 nm) when monitored at respective emission maxima (Fig. S2b; ESI⁺). In order to rule out the possibility of aggregates of 1-4BP in chloroform (0.1-1 μ M), we monitored

the lifetime at the far red shifted emission. Time-resolved measurement at the longer emission wavelength exhibited a



Fig. 1 a) Frontier molecular orbital (FMO) analysis of 1-48P calculated from B3LYP/6-311G**+ level of theory. Lower and upper plots represent the HOMOs and LUMOs respectively; b) Cyclic voltammograms of 1-48P in acetonitrile; c) Absorption spectra of 1-48P; area filled spectrum (grey) represents the absorption spectrum of pyrene²³ and d) Nanosecond transient absorption spectrum of 48P in chloroform.

very short lifetime (<100 ps pulse width at λ_{ex} =375 nm) similar to that observed at the respective emission maxima. An obvious shoulder peak at around 550 nm was observed in the emission spectrum of 2"BP. Wavelength dependent time-resolved fluorescence and excitation spectra invalidates any possibility of aggregates of 2"BP in solution state under these conditions.

As stated above, low Φ_{FI} for 1-4BP could result from an efficient intersystem crossing (ISC) induced by strong mixing of nearly-degenerate singlet and triplet states (Fig. 1d, Table S5, ESI⁺). ISC efficiency of 1-4BP was investigated by employing nanosecond time-resolved absorption spectroscopy (Fig. S3, Table S5; ESI⁺). Upon excitation at 355 nm, 1BP exhibits absorption maximum at 520 nm corresponding to triplettriplet transition of pyrene²⁴ having a lifetime of 2.1 μ s. Similar features for triplet-triplet absorption were also observed for 2-4BP (Table S5; ESI⁺). Estimation of triplet quantum yield (Φ_{T}) of 1BP based on triplet-triplet energy-transfer to β -carotene²⁰ shows a value of 48% (Fig. S4, Table S5; ESI⁺). We observed that Φ_T decreases with increase in number of benzoyl groups (Table S5; ESI⁺). Time-gated emission measurements of 1-4BP in ethanol at 77K show extremely weak phosphorescence when excited at 380 nm (Fig. S2c, Table S5; ESI+). With increase in number of benzoyl groups, systematic red-shift from 510 to 634 nm in the phosphorescence emission maximum was observed. In addition, non-radiative pathways could also operate to cause significantly reduced fluorescence quantum yield in 4BP in chloroform when compared to P. Bond rotations from benzoyl functional groups can contribute to energy dissipative pathways.

Having established the photophysical properties of 1-4BP in solution, further efforts were made to correlate the optical properties in the crystalline state. Detailed analyses of single

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crystal X-ray structure decipher the role of terminal benzoyl groups in impeding the pyrene-pyrene nearest-neighbour interactions in crystalline 1-4BP. Single crystal X-ray analysis of 1BP shows an interplanar distance $(\pi - \pi)$ of 3.50 Å between

the two nearest pyrene units having a transverse slip (along the molecular short axis of the pyrene unit) of 0.69 Å and a longitudinal slip (along the molecular long axis of the pyrene





unit) of 0.93 Å. Observed transverse/longitudinal displacement complements the phenyl rings to adopt an end to face (CH••• π ~2.9 Å) interaction with π -electron cloud of the neighbouring pyrene unit. With increase in the number of benzoyl groups in 2-4BP, a progressive rise in the steric contribution causes an increase in the transverse/longitudinal displacement of the vicinal pyrene units in the crystal structure (Fig. S5&S6, Table S6; ESI⁺). In 4BP, the bulky benzoyl group hampers the strong aggregation, inducing a transverse shift (5.65 Å), prohibiting any π -contacts between neighbouring pyrene units. The longitudinal and transverse offset imparts different degree of orbital overlap between the pyrene units that are separated at their van der Waals distances (ca. 3.35-3.59 Å) in crystalline 1-4BP (Scheme 1, row II, Table S6; ESI+). This intermolecular offset of vicinal pyrene units reduces the $\pi-\pi$ interaction that attributes to the observed decrease in the orbital overlap from 45.92% (1BP) to 0.95% (4BP) (see ESI⁺). Interplanar C–H•••O contacts²⁶ support the pyrene units for an extended interaction along all axis in the crystalline arrangement of 1-4BP (Fig. S7; ESI⁺).

controlled Intrigued bv the sterically longitudinal/transverse shift of intermolecular vicinal pyrene units, further efforts were made to explore the photophysical properties of crystalline 1-4BP. Diverse colour in the crystalline 1-4BP ranging from pale yellow-yellow-orange red (Scheme 1, row III) were observed due to intermolecular offset of vicinal pyrene units in the crystalline state. Diffuse reflectance absorption spectrum of crystalline 1-4BP exhibits a broad band centered around 350-450 nm, with an additional absorption tail extending to 500 nm in 1BP (Fig. 2a, Table S5; ESI+). Presence of benzoyl group(s) results a red-shift in the UV-Vis absorption, for example 114 nm (1BP) and 60 nm (4BP), when compared to crystalline P. Upon excitation at 380 nm, crystalline 1BP exhibits a broad emission band with the maximum centered at 620 nm red-shifted by 148 nm compared to crystalline P. A systematic blue-shift in the emission maximum was observed upon further increase in number of benzoyl groups, when compared to crystalline 1BP (Scheme 1, row III and Fig. 2b&S8, Table S5; ESI⁺). In spite of

the significant π -overlap (π - π ; 39.91%) in crystalline P, a blueshift in the emission wavelength was observed when compared to crystalline 1-4BP. A marked increase in the separation ($d_{\pi-\pi}$ ~ 3.53 Å) between the molecular planes of vicinal pyrene units in crystalline P (Table S6; ESI+) when compared to the crystalline BP derivatives could cause the blue-shift in the emission spectrum. Observed differences in the emission maxima for crystalline 1-4BP could be a combined consequence of different i) degree of π - π overlap and ii) distance between the molecular planes of the adjacent pyrene units. However, contributions from non-nearest neighbour can also contribute to overall electronic coupling that can influence the peak positions in emission spectra. Significant red-shift in the emission wavelength dependent excitation spectra compared to the corresponding steady-state absorption spectra of crystalline 1-4BP suggests the possible ground state interaction between the vicinal pyrene units (Fig. S9; ESI⁺).²⁷ Substantially red-shifted dimer/excimer like emission of 1BP could arise from significant orbital overlap $(\pi-\pi; 45.92\%)$ between the nearest pyrene units. Nearly slipped out (π - π ; 0.95%) pyrene-pyrene stack along the molecular long axis in 4BP results in a monomer-like emission possessing vibronic features.

Upon excitation at 375 nm, picosecond time-resolved fluorescence measurements of crystalline 1BP shows triexponential decay having the lifetime of 2.5 ns (82%), 8.5 ns (12%) and 0.7 ns (6%), when monitored at 620 nm (Fig. S10, Table S5; ESI⁺). Long fluorescence lifetime in crystalline 1BP when compared to that in solution (<100 ps) could arise from excimer/ground state aggregate of neighbouring pyrene units possessing different orbital overlap in the crystalline state. Similarly, crystalline 2-4BP show tri-exponential fluorescence emission profile with a remarkable decrease in the lifetime of the corresponding major component (Fig. 2c, Table S5; ESI⁺). A radiative decay rate constant (k_r) of $1.56 \times 10^8 \text{ s}^{-1}$ and 0.59×10^8 s^{-1} in solution and crystalline state of 1BP, respectively, is estimated (Table S5; ESI⁺). The faster rate of radiative decay in solution vs. crystalline state was similarly observed in 2-3BP. Observed decrease in the rate of radiative decay in crystalline

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1-3BP when compared to solution state indicates the possibility of H-like aggregates and/or excimers of pyrene. Unusual formation of fluorescent H-aggregates were observed earlier in merocyanine dyes by Würthner and coworkers.²⁸ Notably, small π - π contact of vicinal pyrene units in 4BP imparts a monomer-like behavior in the crystalline state (Fig. 2c, Table S6; ESI+), as reported earlier.²⁹ The twisted nature of the benzoyl group(s) with respect to the plane of pyrene chromophore drastically diminishes the aggregation of vicinal pyrene units. Observed similar rate constant in crystalline state and solution state of 4BP confirms the monomer-like behavior in the crystalline state ($k_r \sim 0.59 \times 10^8 \text{ s}^{-1}$; Table S6; ESI+).

Unravelling the processes responsible for crystallization/ aggregation induced emission is vital for the design of new light emitting materials. Recent preliminary theoretical investigations have offered insights on the characteristics of induced CIE in a variety of organic/inorganic chromophores.³⁰ CIE could arise as a consequence of i) electronic interactions^{28,31} arrested (dipolar/excitonic) ii) vibrational/rotational motions;³² and/or iii) reduced solvation³³ in crystalline state. To investigate the extent of vibrationally promoted ISC in monomer vs. dimer states, low-lying excited electronic states of 1BP and 4BP were calculated employing TDDFT method (Fig. S11; ESI+). The energy difference between S_1 and T_1 states in monomeric and dimeric 1BP found to be 1.18 and 0.94 eV, respectively. Notable lowering of T₂ energy state was also observed from monomeric (2.95 eV) vs. dimeric (2.13 eV) 1BP. Similar observations were made in monomeric vs. dimeric 4BP. Non-significant differences in energy gap between the close-lying singlet and triplet energy levels of dimeric vs. monomeric 1BP and 4BP excludes the contribution of vibrational processes in CIE. Restriction of intramolecular rotations offered to the pendent benzoyl groups in the crystalline (dimeric) state of 1-4BP may facilitate enhancement in the fluorescence, consistent with the earlier reports.³⁴ Hence, CIE in 1-4BP could arise due to i) fluorescent H-like excitonic interactions; ii) arrested rotational motion of benzoyl group(s) and/or iii) lack of solvation in the crystalline state (Fig. 2d).

4. Conclusion

In summary, the extent of orbital overlap $(\pi-\pi)$ between vicinal pyrene units in crystalline 1-4BP were regulated by exploiting the steric hindrance offered via successive benzoylation. Progressive increment in the steric hindrance causes an increase in the transverse/longitudinal displacement of the vicinal pyrene units. As a result, a 48-fold reduction in the π -stacking between pyrene units was observed in 4BP with respect to 1BP. Moderating the molecular stacking along with CIE through arrested intramolecular rotations of pendent benzoyl groups may facilitates green-yellow-orange solid-state emitters. Modulating the emission properties of organic crystalline materials by controlling the extent of π -overlap through chemical strategies could lead to the construction of high performance photo-functional materials and devices.

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