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Exciton Isolation in Cross Pentacene Architecture

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ABSTRACT: Null aggregates are elusive, emergent class of molecular assembly categorized as spectroscopically uncoupled molecules. Orthogonally stacked chromophoric arrays are considered as a highlighted architecture for null aggregates. Herein, we unveil the null exciton character in a series of crystalline Greek cross (+) assembly of 6.13-bisaryl substituted pentacene derivatives. Quantum chemical computations suggest that synergistic perpendicular orientation and significant interchromophoric separations realize, negligible long-range Coulombic and short-range charge transfer mediated couplings in the null aggregate. The Greek cross (+) orientation of pentacene dimers exhibit a selectively higher electron transfer coupling with near-zero hole transfer coupling and thereby contribute to the lowering of charge transfer mediated coupling even at shorter inter-chromophoric distances. Additional investigations on the nature of excitonic states of pentacene dimers proved that any deviation from 90° cross-stacked orientation results in the emergence of delocalized Frenkel/mixed Frenkel-CT character and the consequent loss of null exciton/monomer-like properties. The retention of exciton isolation even at short range coupling regime reassures the universality of null excitonic character in perpendicularly cross-stacked pentacene systems. The null-excitonic character was experimentally verified by the observation of similar spectral characteristics in the crystalline and monomeric solution state for 6,13-bisaryl substituted pentacene derivatives. Partitioned influence of aryl and pentacene fragments on interchromophoric noncovalent interactions and photophysical properties respectively resulted in the emergence of pentacene centric Kasha's ideal null exciton, providing novel insights towards the design strategies for cross-stacked chromophoric assemblies. Identifying Greek cross-stacked architecture mediated null excitons with charge filtering phenomenon for the first time in the ever-versatile pentacene chromophoric systems can offer an extensive ground for the engineering of functional materials with advanced opto-electronic properties.

INTRODUCTION

Excitonic communication within self-assembled π -chromophoric systems have been a field of boundless curiosity ever since the pioneering study of dye aggregates by Jelley and Scheibe independently in the 1930s.¹⁻³ Variation in excitonic and electronic coupling via changes in relative spatial orientation and intermolecular distance within the stacked molecular assembly has potent implications on their optical and intrinsic charge transport properties.⁴⁻¹¹ Kasha and coworkers conceived a theoretical relation between the molecular assembly and photophysical properties approximately six decades ago.¹² In the molecular exciton model developed by Kasha, exciton splitting is explained for diverse geometrical arrangements of molecular dimer on the basis of the long-range Coulombic coupling.12 Accordingly, the co-facially stacked and slip-stacked transition dipoles are classified as H- and J-aggregates respectively and have received extensive scientific attention owing to their exceptional electronic/photophysical properties and relative ease of attainability.^{13,14} The model also proposed the possibility of lower exciton splitting for crossstacked dimers having a fixed rotational angle (angle between molecular planes, α) with a null excitonic character for an orthogonal arrangement of molecular transition dipoles. Nevertheless, rational engineering of precise crossstacked assemblies has been a long-standing challenge and demands control over the electronic structure of chromophore and the resultant multifaceted noncovalent interactions, and is therefore essentially not a cakewalk in the field of supramolecular chemistry.¹⁵ As a consequence, the nature of exciton coupling in cross-stacked aggregates is the least understood from a fundamental perspective.¹⁶

Besides cross-stacked aggregates, innovative designs exhibiting nominal excitonic coupling have emerged in recent years.¹⁷ Recently, Xie and coworkers reported remarkably minimal Coulombic coupling in crystalline N,N'bis(4-methoxybenzyl)perylene-3,4,9,10-bis-(dicaboximide) possessing magic angle (slip angle = 54.7°) stacking which they termed as M-aggregate.¹⁸ The theoretical investigations by Spano and coworkers disclosed the importance of short-range charge transfer (CT) interactions, in addition to the Coulombic coupling, originating from HOMO-HOMO and LUMO-LUMO overlap of monomers in describing the nature of excitonic interactions in π -stacked aggregates.¹⁹ The CT-mediated excitonic coupling in molecular aggregates have proven to be highly sensitive wherein a slight variation in slip angle of the molecular dimer reflects oscillating H and J aggregate properties and is attributed to the recurring nodal and antinodal characteristics of interacting frontier molecular orbitals (FMOs).²⁰ The investigation predicted the existence of atypical molecular orientations exhibiting destructive interference of equally strong Coulombic and CT-mediated couplings leading to the null excitonic interactions and thereby a novel epitome of null aggregates.²¹ The proposal was experimentally brought to light by Würthner and coworkers in an exquisite molecular foldamer of perylenediimide (PDI), where equal and opposite Coulombic and charge transfer coupling values resulted in a null aggregate and thereby monomer-like electronic absorption characteristics.²² Lately, the very same PDI-based foldamer (null aggregate) has been found to exhibit singlet fission assisted by the large charge transfer coupling between the chromophores.²³ In a yet another work on intermolecular exciton dynamics, Tamura exploits the diabatization scheme of time-dependent density functional theory to examine singlet exciton coupling, incorporating contributions from Coulomb (Förster) and electron exchange (Dexter) couplings.²⁴ Tamura discusses certain topologies of molecular aggregates causing intermolecular conical intersections with null exciton coupling, specifically T-shape aggregates, boundary of H and J aggregates and canceled coupling to the bright state of H aggregate in a T-shaped trimer.

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Despite the alternate strategies for the construction of aggregates with minimal excitonic interactions, achieving the same through orthogonally cross-stacked architecture remains a formidable yet riveting quest among the scientific community with several groups having verified its existence via a number of experimental and theoretical methods (Table S1).^{15,25-29} The first crystalline Greek cross (+) architecture with null exciton splitting mediated monomeric photophysical properties was reported from our group in 1.7-dibromopervlene-3.4.9.10-tetracarboxvlic tetrabutylester.¹⁶ The cross-stacked assembly additionally demonstrated a unique charge filtering property, opening up the prospect of tailoring the charge transport characteristics along with optical properties via manipulating the rotational angle within the stacked chromophores. In line with our continued efforts in identifying/designing distinct crystalline chromophoric architectures exhibiting fascinating emergent properties, herein we scrutinize a series of all carbon 6,13-bisaryl substituted (4-methylnaphthyl (N₂-P); mesityl (M₂-P); phenyl (P₂-P) groups) pentacene (Ar₂-P) derivatives with crystalline orthogonally cross-stacked chromophoric assemblies possessing null exciton character owing to the negligible Coulombic and CT-mediated couplings (Scheme 1, Figure 1).³⁰⁻³⁵



Scheme 1. (a) Pentacene dimers depicting correlation of Coulombic (J_{Coul}) coupling with rotational angle (α). Large interchromophoric separation lowers charge transfer coupling (J_{CT}). (b) Aryl groups substituted in 6,13 positions of pentacene for attaining the orthogonally cross-stacked architecture.



Figure 1. Orthogonally cross-stacked dimers in crystalline (a) 6,13-bis(4-methylnaphthalen-1-yl)pentacene (N₂-P), (b) 6,13-diphenylpentacene (P₂-P) and (c) 6,13-dimesitylpentacene (M_2 -P). Schematic representation demonstrating intermolecular distance in (d) N₂-P, (e) P₂-P and (f) M₂-P.

The orthogonally oriented pentacene dimers are furthermore found to inherently possess charge filtering phenomenon (selectively higher electron transfer coupling) which turns out to be more intense at shorter interplanar distances (d_i < 5 Å). Thus the sterically bulky aryl substituents at 6,13 positions of pentacene ensure noncovalent interactions mediated orthogonal stacking with substantial interchromophoric separation which lead to near-zero Coulombic and CT-mediated couplings. The study offers potential design principles involving the rational tuning of substituent groups for the construction of cross-stacked aggregates. Achievement of cross-stacked architectures in the multifaceted pentacene systems can possibly have farreaching implications especially in modulating their intrinsic singlet fission capability and/or charge transport properties and subsequently lead to the development of novel optoelectronic properties for device applications.³⁶⁻³⁹

RESULTS AND DISCUSSION

N₂-P, M₂-P and P₂-P were synthesized and crystallized following the procedures reported by Nuckolls and Chi (Scheme S1, Table S2).^{40,41} The 6,13-bisaryl substituted pentacene (Ar₂-P) derivatives crystallized in the tetragonal crystal system with space groups $I4_1/a$ (N₂-P, and M₂-P), and $P4_1/a$ (P₂-P). The analysis of single crystal X-ray structure of the three pentacene derivatives revealed the unique Greek cross (+) architecture in which the nearest neighbours are orthogonal with respect to the long axis of pentacene forming a columnar organization (Figure S1). The crystal structure of the three Ar₂-P derivatives show a bend over the long axis of pentacene in the crystal structure (Figure S2). A comprehensive analysis of the single crystal X-ray structure of N₂-P reveals two types of dimers in the columnar cross-stacks with intermolecular distances of 4.74 Å (dimer A) and 7.60 Å (dimer B) (Figures S3a, b). Close-packing analysis in crystalline N₂P depict inter-stack C–H···C (d_{C−H···C} = 2.84 and 3.00 Å) and C···C (d_{C···C} = 3.22 Å) and intra-stack C–H···C ($d_{C-H···C} = 2.95$ and 2.98 Å) interactions between naphthalene group and pentacene moiety along with inter-stack C···C ($d_{C···C} = 3.40 - 3.80$ Å) interactions between naphthalene entities (Figures S3c,

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S4a, S5). The cross-stacked array of M₂-P also shows two 1 dimers with small variance in the intermolecular distance 2 $(d_i = 5.99 \text{ and } 6.18 \text{ Å})$. The close-packing in M₂-P exhibits 3 inter-stack C–H···C ($d_{C-H··C} = 2.84$ and 2.88 Å) and within the stack C–H···C (d_{C-H··C} = 2.24 to 2.86 Å) interactions (Figure 4 5 S4b, S6). Crystalline P2-P reveals inter-stack C-H···C (dC-H···C = 2.13 - 2.79 Å) and intra-stack C–H···C ($d_{C-H···C}$ = 2.85 and 6 2.87 Å) interactions with stacked dimers possessing 7 interchromophoric distance of 4.90 Å (Figures S4c, S7). 8 Centroids of monomers in P2-P dimer have a slight 9 displacement of 0.4 Å from each other when viewed along 10 the cross-stack implying a slight deviation from ideal Greek 11 cross (+) architecture (Figure S8). The sterically bulky aryl 12 substituents in pentacene induce interchromophoric 13 C–H…C interactions directing the orthogonal cross-stacked 14 orientation at a considerable interplanar distance $(d_i \ge 4.74)$ 15 Å) within the stacked dimers of crystalline Ar₂-P systems 16 (Figure S4).

17 Noncovalent interaction analysis (NCI), Hirshfeld surface 18 (HS), and truncated symmetry adapted perturbation theory 19 (SAPT(0)) based analyses were performed to gain further insights into the weak intermolecular forces governing the 20 formation of Greek cross (+) pentacene molecular assem-21 bly.⁴²⁻⁴⁴ NCI plot conferred the noncovalent interactions in 22 Ar₂-P systems by analysing the topology of the electron den-23 sity, where the weak stabilising interacting region is 24 marked as a green disk (Figure S9). NCI calculations di-25 vulged the dominating role of intermolecular C-H···C inter-26 actions between the substituted aryl groups and the penta-27 cene core in orchestrating the perpendicularly cross-28 stacked arrangement of pentacene units in the crystal pack-29 ing of Ar₂-P derivatives. Hirshfeld surface and two-dimen-30 sional (2D) fingerprint analyses were carried out to obtain 31 a quantitative view of the role of weak intermolecular inter-32 actions in generating the Greek cross-stacked assembly 33 (Figure S10). The high value of the ratio of %C-H···C to %C···C ($\rho > 4$) obtained further substantiate the prevailing 34 influence of the edge-to-face C-H···C interactions in 35 directing the crystal packing (Table S3).^{45,46} A quantitative 36 assessment of the total interaction energy and contributing 37 noncovalent components of the stacked dimers were per-38 formed using the SAPT(0) analysis (Table S4). M₂-P dimer 39 exhibited a dispersion dominated stabilization of -64.4 40 kJ/mol. N₂-P and P₂-P dimers reflected an enhancement in 41 dispersion component leading to higher stabilization 42 $(E^{SAPT(0)} = -98.8 \text{ and } -93.8 \text{ kJ/mol respectively})$ in compari-43 son with M₂-P having larger interplanar/intermolecular 44 distance. The negative values obtained for the total SAPT(0) 45 energy with dispersion interaction as the major patron val-46 idates the stability of the Greek cross (+) Ar₂-P dimers.^{44,47}

Having rationalized the evolution of Greek cross-stacked networks in crystalline Ar₂-P derivatives, we ventured to explore the nature of excitonic interactions intrinsic to the spatial orientation of chromophores. The excitonic coupling within the cross-stacked dimer was theoretically examined by evaluating the contributions from both long-range and short-range effects. The long-range Coulombic coupling originating from the interaction between molecular transition dipole moments is expressed by the dipole-dipole interaction given as:^{48,49}

$$I_{coul} = \frac{1}{4\pi\varepsilon_0} \kappa \frac{|\mu_1||\mu_2|}{R^3}$$
(1)

wherein $|\mu_1|$ and $|\mu_2|$ correspond to the magnitudes of the transition dipoles of chromophore 1 and 2, R is the interchromophoric separation and κ conform to the orientation factor. However, Coulombic interaction has been found to involve multipole couplings along with the basic dipole-dipole approximation for short to intermediate interchromophoric distances.⁴⁹ Herein, the Coulombic coupling was calculated by employing electronic energy transfer (EET) analysis available in Gaussian 16 (See the Supporting Information). N₂-P (dimer A and B) and M₂-P dimers exhibited *J_{coul}* values of 0.10 cm⁻¹ and -0.02 cm⁻¹ respectively, while the phenyl substituted P2-P dimer was characterized with a *Icoul* value of -12.35 cm⁻¹. The negligible magnitudes of J_{Coul} obtained for cross-stacked dimers of Ar₂-P derivatives (Table 1) reinforce the hypothesis of minimum Coulombic coupling within stacked chromophoric assemblies comprising of orthogonally aligned transition dipoles (Figure S11).²² The short-range exciton coupling stemming from the degree of overlap of wavefunctions on proximal molecules have a crucial role in defining the excitonic interaction and is determined as:19,50

$$J_{CT} = \frac{-2t_e t_h}{E_{CT} - E_{S_1}}$$
(2)

where, t_e and t_h are the electron and hole transfer coupling which depend on LUMO-LUMO and HOMO-HOMO orbital overlap of the monomers respectively, E_{CT} is the energy of the charge transfer state, and E_{S_1} is the energy of first Frenkel exciton state. The total coupling between neighbouring molecules can be represented as:²¹

$$J = J_{Coul} + J_{CT} \tag{3}$$

The hole and electron transfer couplings in cross-stacked dimers of N₂-P, M₂-P and P₂-P were calculated (Table 1). We further proceeded to calculate the J_{CT} value using the equation (2). The energy of the E_{CT} is usually hundreds of meV higher than the E_{S_1} states for polyacene molecular crystals.⁵⁰ The energy difference between charge transfer state (E_{CT}) and local Frenkel exciton state (E_{S_1}) for P₂-P (E_{CT}- E_{S_1} = 5968.5 cm⁻¹) obtained from a previous report by Yost. et al. was used for calculating J_{CT} of Ar₂-P derivatives.³⁸ The resultant low magnitude obtained for J_{CT} (Table 1) restates insignificant nature of charge transfer coupling in the cross-

Table 1. Calculated Coulombic coupling (*J*_{coul}), hole (*t*_h) and electron (*t*_e) transfer couplings, and short range exictonic coupling (*J*_{cr}) for orthogonally cross-stacked dimers of N₂-P (A and B), M₂-P and P₂-P.

Molecule	JCoul	t h	te	Jcт
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
N2-P (A)	0.102	-0.008	-59.871	-1.6x10 ⁻⁴
N2-P (B)	0.099	-0.029	7.662	0.74x10 ⁻⁴
M ₂ -P	-0.019	0.123	116.265	-4.7x10 ⁻³
P ₂ -P	-12.348	93.738	70.493	-2.214

stacked dimers of Ar₂-P derivatives. Thus, Greek crosssystems exhibit exciton isolation owing to the negligible Coulombic and CT-mediated couplings.

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Rotational angle dependent Coulombic coupling was probed for M₂-P dimer having the intermolecular distance of 5.99 Å to assess the effect of spatial orientation between the transition dipoles on the Coulombic coupling over the fixed distance (Figure 2a). The M2-P dimer with a rotational angle of 90° has J_{Coul} in the order of 10⁻² cm⁻¹. The J_{Coul} drastically increased to 8.07 cm⁻¹ for rotation of a molecule with respect to the other about an angle of 5⁰ from the initial 90° cross architecture. A steady increment of Jcoul with the decrease of rotational angle is observed, which includes a maximum value of 202.45 cm⁻¹ for the dimer with the rotational angle of 40° and thereby belonging to a relatively stronger Coulomb-coupled regime. The results of the rotational angle dependent investigation of the Coulombic coupling in M₂-P dimer with a separation of 5.99 Å can be applied to N₂-P and P₂-P, which have a similar carbon backbone and shorter interchromophoric distance. Thus, the negligible magnitude of Coulombic coupling arises from the orthogonal orientation of the transition dipoles of the homo-dimers.

21 Higher magnitude of t_e compared to t_h reflects charge fil-22 tering capability for M₂-P and N₂-P cross-stacks. To explore 23 the charge filtering effect in greater detail, the mesityl 24 groups of M₂-P dimer were replaced by H atom, and varia-25 tion in *t_e* and *t_h* were examined as a function of interplanar 26 distance (d_i) between the chromophores. The exponential 27 reduction of charge transfer coupling with an increase in in-28 terplanar spacing was previously reported by Bredas and coworkers in cofacial dimers.⁵¹ Our investigation in cross-29 stacked pentacene reinforces the relation for both hole and 30 electron tranfer couplings with a fine exponential fit (Fig-31 ures 2b, S12a). Cross-stacked pentacene dimer is observed 32 to possess a considerably lower charge transfer coupling (t_e 33 = 225.13 cm⁻¹ and t_h = 1.55 cm⁻¹ for d_i = 3 Å) than the previ-34 ously investigated cofacial orientation ($t_e \approx 4800 \text{ cm}^{-1}$ and t_h 35 \approx 3600 cm⁻¹ for d_i = 3.3 Å) which can be attributed to the 36 lower acene overlap area and consequently lower orbital in-37 teraction in the former.⁵¹ Our study also revealed a selec-38 tively higher t_e for orthogonally arranged pentacene chro-39 mophores while Greek cross-stacked 1,7-dibromoperylene-40 3,4,9,10-tetracarboxylic tetrabutylester reported earlier by 41 us was biased towards higher *t*_h.¹⁶ The preexponential con-42 stant of electron transfer coupling, Ae of the perpendicularly cross-stacked pentacene dimer was found to be 433 times 43 higher than that of hole transfer coupling, A_h. The ratio of 44 electron to hole (t_e/t_h) transfer integrals rises at closer in-45 terplanar distances (d_i < 5 Å, Figure S12b). In an attempt to 46 comprehend the role of the Greek cross (+) architecture in 47 the emergent charge filtering phenomenon, computed rota-48 tional angle dependent charge transfer couplings in penta-49 cene dimer were assessed at the interplanar distances of 6 50 Å and 4 Å (Figure S13). The magnitude of both t_e and t_h were 51 found significant at lower α values for d_i = 4 Å, suggesting 52 greater orbital interaction between the monomers. The t_e 53 was found to be slightly higher than t_h at α values ranging 54 from 0-30° with the trend reversing for α values within the 55 limits of 35-85° (Figure S14). The highest values of t_e/t_h 56 were obtained for the orthogonally cross-stacked 57



Figure 2. (a) The variation of modulus of Coulombic coupling $(|J_{Coul}|)$ with respect to the rotation angle (α) between the monomers of M₂-P separated by 5.99 Å. (b) The exponential dependence of charge transfer coupling to the interplanar distance (d_i). C₁ = -0.03 cm⁻¹, C₂ = -2.44 cm⁻¹, A_h = 73.17 cm⁻¹, A_e = 31690.86 cm⁻¹, R_h = 1.28 and R_e = 1.64. (c) (i) HOMO of pentacene exhibiting long molecular axis node and resulting node-antinode arrangement in the dimer and (ii) LUMO of pentacene depicting absence of long axis node which results in antinode-antinode interactions.

orientation (α =90°) along with marginal t_e/t_h values at other angles (Figure 3a). The striking selectivity for electron transfer coupling at the perpendicularly stacked arrangement can be traced down to the node-antinode patterns in the frontier molecular orbitals of the pentacene and Ar₂-P

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systems (Figures 2c, S14).⁵¹ The HOMO, which determines the hole transfer coupling, of pentacene has a characteristic node along the long molecular axis. The overlap between two monomer orbitals is limited to the central acene of pentacene backbone in the cross-stacked orientation, where the antinodes on 6, 13-positions of one pentacene is aligned along the long molecular axis node of the other giving rise to negligible th values for Greek cross-stacked dimers of pentacene. The shift from perfect Greek cross (+) alignment in P₂-P cross dimers plausibly resulted in the increased hole transfer coupling observed for the system. The absence of 10 long molecular axis node in LUMO leads to better electron 11 transfer coupling. Thus, the unprecedented potential of 12 Greek cross-stacked pentacene dimers for causing the 13 charge filtering phenomenon and subsequent nullification 14 of *I*_{CT} is revealed.

15 The impact of charge filtering phenomenon in the charge 16 transport characteristrics of Ar₂-P systems is explored by 17 calculating anisotropic charge mobility of Ar₂-P crystals using semi-classical Marcus theory employing the method de-18 veloped by Han and coworkers.52 The crystallographic c-19 axis along the cross-stacked direction is taken as the princi-20 ple axis for the anisotropic mobility analysis (Figures 3b-c). 21 The reorganization energies in the three Ar₂-P derivatives 22 are in line with the bare pentacene backbone, with lower 23 value for hole and higher value for electron transport ($\lambda_h <$ 24 λ_e). Selective electron mobility is observed along the cross-25 stacking direction for M₂-P (μ e =1.25 x 10⁻³ cm²V⁻¹s⁻¹, μ h = 26 2.38 x 10⁻⁶ cm²V⁻¹s⁻¹) and N₂-P (μ_e = 3.19 x 10⁻⁷ cm²V⁻¹s⁻¹, μ_h 27 = $1.95 \times 10^{-8} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) crystals and can be attributed to the 28 insignificant t_h evaluated for the cross-stacked dimer. Crys-29 talline P₂-P depicts ambipolar mobility ($\mu_e = 3.31 \times 10^{-4}$ 30 $cm^{2}V^{-1}s^{-1}$, $\mu_{h} = 4.09 \times 10^{-4} cm^{2}V^{-1}s^{-1}$) along cross-stacking axis 31 which is consistent with the nearly similar magnitudes of te 32 and t_h for the cross-stacked dimers of P₂-P. Maximal values 33 of charge transport for crystalline Ar₂-P systems are obtained along the direction nearly perpendicular to the cross-34 stacking axis with M₂-P and P₂-P systems exhibiting ambi-35 polar character (Figures 3d, S15). 36

In a bid to identify the relevance of symmetric 'Greek' cross dimer in inducing null exciton coupling, Coulombic and charge transfer couplings of orthogonal pentacene dimer from Greek cross to Latin cross and T-shape orientations were evaluated at an intermolecular distance of 4 Å. Fascinatingly, the new asymmetric dimer orientations also vielded minimal excitonic coupling with moderate rise in *I*_{Coul} for progressive translational shift of one of the monomers along direction of its short axis (Figure S16). The study points toward the potential of Latin cross and T-shape stacked architectures in addition to the electron 'Greek' cross orientation in causing null exciton splitting, however, remains to be experimentally identified.

Thus, the 90° dimer orientation stands out from any other angular dimers in terms of charge transfer coupling and and photoexcited state (null exciton interactions) properties. Hence, it is imperative to understand the inherent nature of excited states of the dimers at different rotational angles. The exciton characteristics of rotational angle dependent dimer orientations ($d_i = 6 \text{ Å}$) were probed utilizing the fragment-based excited state analysis developed by Plasser,



Figure 3. (a) t_e/t_h at various rotational angle (α) of pentacene dimer, (b) M₂-P crystal viewed along crystallographic *c*-axis, (c) M₂-P crystal viewed along plain of interest (*bc* plane), the direction of principle axis (c-axis) with anisotropic mobility pattern superimposed and (d) corresponding anisotropic hole (μ_h , violet) and electron (μ_e , orange) mobility.

implemented using TheoDORE (See Supporting Information).^{53–55} The participation ratio (PR) describes the extent of delocalization of the excitation in line with the number of fragments. In the case of pentacene dimers, each pentacene monomer is considered as a fragment. Thus, the P_R will have magnitude ranging from 2 (delocalized on 2 fragments) to 1 (localized on 1 fragment). The charge transfer character (CT) of the excited state is defined by the CT value which can vary from of 1 (full CT character), to 0 (pure Frenkel nature). POS value qualitatively gives the contributions of monomer 1 and monomer 2 towards the excitation. At 6 Å, the 90° cross-stacked dimer has two localized nearly degenerate Frenkel states (S₁ and S₂ states with P_R = 1, CT = 0)

in each fragment/monomer (S₁ with POS = 1 and S₂ with POS = 2) with equal oscillator strengths (f = 0.0549, Figures 4a and 4c) (Table S5, Figure S17, S18). As the α value deviates from 90°, the localized Frenkel excitations in each monomer undergo mixing and split to form two delocalized Frenkel excitons. At α = 80°, the S₁ and S₂ states are delocalized Frenkel excitons with S₁ state having higher monomer 1 character (P_R = 1.51, POS = 1.215), and S₂ state possessing greater monomer 2 character (P_R = 1.51, POS = 1.785). In addition, the oscillator strength of S₁ state decreases and S₂ state increases in comparison to that of the orthogonally oriented dimer (Figure 4c, at d_i = 6 Å). The trend continues



Figure 4. (a) Exciton analysis of pentacene dimer at 6 Å (long range) interplanar distance with variation in dimer rotation (α): (i) Excitation energies of S₁, S₂, S₃, S₄ states and corresponding (ii) P_R, (iii) POS and (iv) CT values. The yellow region depicts the splitting of Frenkel states due to long range Coulombic coupling (J_{Coul}), (b) Exciton analysis of pentacene dimer at 4 Å (short range) interplanar distance with variation in dimer rotation (α): (i) Excitation energies of S₁, S₂, S₃, S₄ states and corresponding (ii) P_R, (iii) POS and (iv) CT values. The additional short range charge transfer coupling (J_{Cr}) effects are observed from $\alpha < 20^{\circ}$, (c) The computed UV-vis absorption spectra for S₀ to S₁ and S₀ to S₂ transitions as α deviates from 90° to 0° and (d) Hole and electron isosurface (for $\alpha = 90^{\circ}$, 60°, 30° and 0°) at 4 Å interplanar distance for S₀ to S₁ transition.

up to $\alpha = 0^{\circ}$ and can be correlated to the increase in Cou-1 lombic coupling with decrease in α values. At $\alpha = 0^{\circ}$, each 2 monomer has almost equal contribution to the delocalized 3 Frenkel states ($P_R = 1.97$, POS = 1.44 and 1.55 for S_1 and S_2) 4 and the transition to S_1 state becomes forbidden (f = 0) 5 while to that of S_2 state tends to be more allowed (f = 0.133). 6 Thus, the cofacially stacked pentacene dimer ($\alpha = 0^{\circ}$) behaves as an ideal H-aggregate. The description is pictorially 7 depicted using electron-hole correlation plot (Figure S17a). 8 Hence, at 6 Å interplanar distance, the 90° cross-stacked 9 orientation is the only dimer arrangement where the exci-10 ton behavior retains independent monomer nature (null ex-11 citon). The S₃ and S₄ states of all the above pentacene dimers 12 are degenerate forbidden pure CT states ($P_R = 1$, CT = 1, POS 13 = 1.5), where the hole is localized in one fragment, and elec-14 tron is localized on the other. There is no mixing between 15 the CT states or CT and Frenkel states due to the high inter-16 planar distance $(d_i = 6 \text{ Å})$ and the consequent negligible 17 short-range coupling.

To understand the influence of short range coupling on the 18 nature of excitons in cross-stacked dimer, we extended the 19 above investigations for dimers at $d_i = 4$ Å (Table S6, Figures 20 4b, S17b). The perpendicularly stacked pentacene dimer 21 displayed an excitonic behavior identical to that at 6 Å in-22 terplanar distance with monomer like localised Frenkel ex-23 citon states exhibiting equal oscillator strengths for S₁ and 24 S_2 , and pure CT character for S_3 and S_4 . Dimers with α val-25 ues ranging from 80° to 30° exhibit delocalized Frenkel 26 character for S₁ and S₂ states similar to that at $d_i = 6$ Å while 27 S₃ and S₄ possess CT character. However, for dimers with 28 α values varying from 20° to 0°, strong mixing of the Fren-29 kel and CT states in S1 and S4 is observed (Figure S17b), 30 leading to significant energy splitting. The coupling be-31 tween Frenkel and CT states occurs when there is signifi-32 cant HOMO-HOMO (t_h) and LUMO-LUMO (t_e) orbital overlap 33 between the monomers. Thus, the higher mixing of Frenkel and CT states at lower α values can be attributed to the sub-34 stantial te and th values of the corresponding dimer orienta-35 tions (Figure S14). The S₂ and S₃ exhibit the delocalized 36 Frenkel and delocalized CT characters respectively. The co-37 facially stacked pentacene dimer with S2 state posessing de-38 localized Frenkel character as the only bright state among 39 the first four excited states, has the features of a wavefunc-40 tion overlap (WFO) coupled H-aggregate.²⁰ Hence, the or-41 thogonally cross-stacked orientations falling within the 42 short-range coupling regime also succeed in preserving the 43 monomer-like exciton characteristics setting itself uniquely 44 apart from other angular dimers.

45 The computed UV-vis absorption spectra for S_0 to S_1 and 46 S_0 to S_2 transitions graphically illustrated the decreasing 47 and increasing oscillator strength of the excitations respectively, and the breakdown of S₁-S₂ degeneracy for dimer ori-48 entations as the rotational angle (α) varies from 90° to 0° 49 (Figure 4c). The nature of the excitations for the cofacial and 50 orthogonally oriented stacked pentacene dimers were also 51 explored via hole-electron isosurface analyses (Figures 4d, 52 S18, S19). The localized Frenkel/pure CT states depicted 53 containment of hole-electron distribution on the same/sep-54 arate fragments. The excitations possessing delocalized 55 Frenkel, delocalized CT or mixed Frenkel-CT character ex-56 hibited delocalization of hole-electron isosurface over both 57 the fragments. 58

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Nature of the first four excited states of Ar₂-P derivatives were also investigated using TheoDORE. Cross-stacked M₂-P and N2-P dimers exhibited majorly localized Frenkel character { $P_R(M_2-P) = 1.44(S_1) \& 1.30(S_2)$; $P_R(N_2-P) = 1.02(S_1)$ & $1.27(S_2)$ and identical oscillator strength for the nearly degenerate S_1 and S_2 states while the degenerate S_3 and S_4 states possessed pure CT nature (CT = 0.01 for S₃ and S₄ state in M₂-P and N₂-P cross stack) (Table S7). The first two excited states of cross-stacked P2-P dimer displayed a moderately delocalised Frenkel nature $\{P_R = 1.79(S_1) \& 1.79(S_2)\}$ and can be attributed to the relatively higher *J*_{Coul} estimated for P2-P dimer when compared to that obtained for M2-P and N₂-P counterparts. The S₃ and S₄ states demonstrated pure CT character. The hole-electron isosurface analyses of the S₀ to S₁ transition of cross-stacked dimers of Ar₂-P systems depicted localization of hole-electron distribution in a single molecule for M2-P and N2-P and moderate level of delocalization within the dimers for P₂-P. This is consistent with the isolated and delocalised nature of the Frenkel excitations respectively for the corresponding systems (Figure S20). The orbitals involved in the allowed electronic transitions for N₂-P, M₂-P and P₂-P (Figure S21) are mainly observed to be the frontier molecular orbitals (FMO) localized on the pentacene fragment of the substituted monomers. Hence, the low energy S_0 to S_1 and S_0 to S_2 transitions can be attributed to the pentacene backbone with negligible interference from the substituted Ar groups. The FMO analysis on the Ar₂-P revealed degenerate/nearly degenerate HOMO. HOMO-1 and LUMO. LUMO+1 levels due to the minimal interaction within the dimers in the Greek cross (+) architecture. The wavefunction of orbitals are localised or delocalised over the pentacene backbone of single or both the fragments respectively in accordance with their t_h (for HOMO and HOMO+1) and t_e (for LUMO and LUMO+1) values.

Spectroscopic investigations performed in the dilute solution (chloroform) and crystalline state of the Greek cross stacked pentacene derivatives provided experimental verification for the intriguing null exciton splitting. The fluorescence excitation and emission spectra (See Supporting Information⁵⁶) of crystalline Ar₂-P systems were found to preserve the characteristic features of the fluorescence excitation and emission spectra in corresponding monomeric solutions (Figures 5, S22). The monomeric P₂-P in chloroform exhibited fluorescence excitation spectrum with structured band at 450-650 nm region and vibronically resolved emission spectrum with peaks at 613 and 661 nm. The fluorescence excitation and emission spectra of crystalline P2-P showed remarkable resemblance to pentacene-centric excitation and emission spectra recorded in solution state. Furthermore, crystalline M2-P and N2-P also showed unperturbed spectroscopic properties as that of the corresponding monomeric solution (Figures S22, S23), substantiating the theoretical observation of exciton isolation.

CONCLUSIONS

In conclusion, we have introduced a series of 6,13-bisaryl substituted pentacene derivatives forming the distinct Greek cross (+) architecture with appreciable interchromophoric separation ($d_i = 4.74 - 5.99$ Å) in the crystalline state.



Figure 5. Fluorescence excitation (solid) and emission (broken) spectra of P₂-P in dilute chloroform solution (blue) and crystalline state (red).

Crystal structure examination, NCI analysis, Hirshfeld surface analyses and SAPT(0) evidenced the preponderating role of intermolecular noncovalent C-H···C interactions between the aryl substituents and the pentacene backbone in the emergence of crystalline cross-stacked columnar edifices. The orthogonally oriented dimeric systems demonstrated exceptionally exiguous excitonic communication owing to the negligible contributions from long-range Coulombic (*I*_{coul}) and short-range charge transfer exciton (*I*_{CT}) mediated couplings as evaluated exploiting advanced computational methods. The rotational angle dependent Coulombic coupling calculations provided significant values for lower values of rotational angle ($\alpha < 70^{\circ}$) manifesting impeccable evidence for the ability of Greek-cross (+) architecture in lowering long-range Coulombic coupling. The pentacene cross-stacks impart selective electron tranfer coupling even at shorter interchromophoric distance ($d_i < 5$ Å), owing to the long molecular axis node in HOMO of the pentacene backbone hindering efficient HOMO-HOMO interaction and effectively lowering the hole transfer coupling, and hence assist in the filtering of charge transfer coupling. The Greek-cross oriented pentacene dimers exhibited localised Frenkel character and equal oscillator strength for the first two degenerate excited states. Deviation from $\alpha = 90^{\circ}$ resulted in the emergence of delocalised Frenkel $(I_{coul}, \text{ for } d_i =$ 6 Å, $\alpha = 80^{\circ}-0^{\circ}$ and $d_i = 4$ Å, $\alpha = 80^{\circ}-30^{\circ}$) and mixed Frenkel-CT ($I_{coul} + I_{CT}$, for d_i = 4 Å, α = 20°-0°) character along with the breakdown of degeneracy, and decreasing and increasing oscillator strengths for S₁ and S₂ states, respectively.

45 The calculated UV-vis absorption spectra and FMO analy-46 sis of the Ar₂-P monomers indicated the localization of the 47 allowed S₀ to S₁ transition on the pentacene backbone. Char-48 acteristic signatures of the fluorescence excitation and 49 emission spectra of Ar₂-P in the monomeric solution-state 50 were retained in the corresponding crystal state providing experimental validation for exciton isolation in crystalline Ar₂-P derivatives. Thus, the substituted bulky Ar groups dictate the ground state intermolecular interactions facilitating the perpendicular alignment of molecular transition dipoles at a considerable separation in the crystal state while the pentacene moiety reigns over the excited state properties pinpointing towards the elegance of the material design. Greek cross (+) pentacene aggregates impede Coulombic coupling and facilitate, charge filtering and enhanced interchomophoric distance mediated, interception of charge transfer coupling, exemplifying an exceptional design strategy for the materialization of Kasha's classic null exciton splitting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

Experimental and computational methods, CCDC number, tables (Tables S1–S7) and figures (Figures S1–S23) (PDF) Crystallographic data for N₂-P, M₂-P (CIF).

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Notes

The authors declare no competing financial interest.

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