Structure–Property Relationships

Relationship between Molecular Stacking and Optical Properties of 9,10-Bis((4-N,N-dialkylamino)styryl) Anthracene Crystals: The Cooperation of Excitonic and Dipolar Coupling

Feng Li,^[a] Na Gao,^[a] Hai Xu,^[a] Wei Liu,^[b] Hui Shang,^[a] Wenjun Yang,^[b] and Ming Zhang^{*[a]}

Abstract: Five 9,10-bis((4-*N*,*N*-dialkylamino)styryl) anthracene derivatives (DSA-C1–DSA-C7) with different length alkyl chains were synthesized. They showed the same color in dilute solutions but different colors in crystals. The absorption, photoluminescence, and fluorescence decay indicate that there exist both excitonic and dipolar coupling in crystals of DSA-C1–DSA-C7. X-ray crystallographic analysis revealed that all the crystals belong to the triclinic space group $P\bar{1}$ with one molecule per unit cell and that the molecules in every crystal have the identical orientation. This offers ideal samples to investigate the impact of the molecule

Introduction

Organic single crystals constructed by π -conjugated molecules have attracted a great deal of interest in the field of optoelectronic devices such as optically pumped lasers,^[1-3] field-effect transistors (FETs),^[4-7] electroluminescence (EL) devices,^[8,9] and photovoltaic cells^[10-12] due to their high thermal stability, their highly ordered structure, and their high carrier mobility. Generally, optical and electrical properties of organic crystals like absorption, luminescence, and carriers mobility are governed not only by the structure of the monomolecules, but also by their stacking patterns, which can be influenced strongly through noncovalent intermolecular interactions such as hydrogen bonding, $\pi-\pi$, C–H…pi interactions, etc.^[3,13-29] Thus, understanding and controlling molecular stacking patterns are fundamental issues for obtaining the desired optical and electrical properties of organic crystals.^[18-21,23,30-37] There are many publications dealing with the relationship between molecular stacking and optical properties. For instance, Bao et al. reviewed strategies to tune molecular packing of organic semiconductors and their impact on charge transport.^[38] Wang et al. re-

[a]	Prof. F. Li, N. Gao, Prof. H. Xu, Dr. H. Shang, Prof. M. Zhang
	State Key Laboratory of Supramolecular Structure and Materials
	Jilin University, 2699 Qianjin Avenue, Changchun (P.R. China)
	E-mail: zhming@jlu.edu.cn

[b] Dr. W. Liu, Prof. W. Yang Key Laboratory of Rubber-plastics of Ministry of Education Qingdao University of Science & Technology 53-Zhengzhou Road, Qingdao, 266042 (P.R. China) lar stacking on the optical properties of the crystals. For the first time, the cooperation of excitonic and dipolar coupling has been comprehensively studied, and the contribution to the spectral shift from the excitonic and dipolar couplings quantitatively obtained. The experiments of amplified spontaneous emission (ASE) together with measurements of the quantum efficiency further confirmed this interpretation. The results suggest that the excitonic and dipolar couplings between the adjacent molecules are both important and jointly induce the spectral shifts of the crystals.

ported hydrogen-bonded stacking-induced emission of aminobenzoic acid compounds.^[14, 29, 39] Kitamura et al. could tune the solid-state optical properties of tetracenes by the length of the alkyl side chain.^[19] Mizuguchi et al. investigated the correlation between the spectral shifts of crystals and the structure of crystals of diketopyrrolopyrrole pigments and quinacridone derivatives.^[20,21] Ma et al. found a stable cross-stacking mode in the crystalline state of 2,5-diphenyl-1,4-distyrylbenzene, which has a high fluorescence quantum yield.^[27] Saito et al. controlled the solid-state properties of π -conjugated systems by macrocyclic restriction with flexible alkylene linkers.^[25] Das et al. studied the correlation between molecular packing and the solid-state photophysical properties of a series of diphenyl butadiene derivatives.^[24,40,41] Gierschner et al. and Park et al. investigated the consequences of different packing motifs in single crystals of a series of distyrylbenzene derivatives on the photophysical and laser properties.^[42-44]

In general, there are two types of coupling that can affect the optical properties of organic crystals. One is the excitonic coupling, that is, an excimer, which is referred to the dimers that exist only in the excited state and the ground state of the pair is dissociative. The other is the dipolar coupling, that is, Haggregate or J-aggregate formation that describes the situation in which two or more identical molecules are close to each other in a special spatial arrangement.^[30,32] Up to date, most of the works about the structure–property relationship of organic crystals focused either on the excitonic coupling or on the dipolar coupling, and the works studying the cooperation of both couplings are rare. Actually, some molecules can form H-aggregats in crystals with a blue-shifted absorption but a red-shifted fluorescence.^[42,45] In this work, we report our re-

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201402369.





Figure 1. Absorption and PL spectra of the 9,10-bis((4-N,N-dialkylamino)styryl) anthracene derivatives (DSA-C1–DSA-C7) in dilute dichloromethane solution. The inset shows the molecular structural formulas of DSA-C1–DSA-C7.

sults on 9,10-bis((4-*N*,*N*-dialkylamino)styryl) anthracenes with different length of the alkyl chain (DSA-C1–DSA-C7), where the number in the dubbed names represents the amount of carbon atoms in each tail chain (inset of Figure 1). They have the same optical properties in solution but different optical properties in the crystal state. Our study about the molecular stacking and optical properties of crystals of compounds DSA-C1–DSA-C7 now shows that the cooperation of excitonic coupling and dipolar coupling induces the observed spectral shifts.

Results and Discussion

Synthesis and optical properties in solution and crystal form

The five compounds were synthesized according to the reported procedures and the details can be found in the Supporting Information.^[26]

DSA-C1–DSA-C7 possess a pale yellow color in diluted dichloromethane solution as shown in Figure 2a, and their absorption and photoluminescence (PL) spectra are provided in Figure 1. As can be seen, the absorption and PL spectra of these compounds in dilute solution are almost the same, which indicates the single-molecule properties of the compounds come from the 9,10-bis((4-*N*,*N*-dialkylamino)styryl) anthracene, and the alkyl chains at the end do not participate in the absorption and emission processes.

Five single crystals of DSA-C1–DSA-C7 have been successfully obtained by the vapor diffusion method in which dichloromethane was used as the favorable solvent and methanol as the unfavorable solvent. Under the irradiation of UV light at $\lambda = 365$ nm, the single crystals of DSA-C1–DSA-C7 show different colors ranging from yellow to red, as displayed in Figure 2b. The PL spectra of the crystals are also depicted in Figure 2. The peak positions are in the following order: DSA-C3 ($\lambda = 565$ nm) < DSA-C4 ($\lambda = 567$ nm) < DSA-C6 ($\lambda = 580$ nm) < DSA-C1 ($\lambda = 593$ nm) < DSA-C7 ($\lambda = 609$ nm). It is difficult to obtain the absorption spectra of crystals directly, therefore, we



European Journal

Full Paper

Figure 2. PL spectra of 9,10-bis((4-*N*,*N*-dialkylamino)styryl)anthracene crystals (DSA-C1–DSA-C7) and images of a) dilute dichloromethane solution (\blacksquare = DSA-C1, \bullet = DSA-C3, ▲ = DSA-C4, \blacktriangledown = DSA-C6, and \blacktriangleleft = DSA-C7) and b) crystals (under UV light of λ = 365 nm).



Figure 3. Absorption spectra of the 9,10-bis((4-*N*,*N*-dialkylamino)styryl) anthracenes in films. ■ = DSA-C1 (λ = 300, 339, 452 nm), ● = DSA-C3 (λ = 259, 282, 338, 450 nm), ▲ = DSA-C4 (λ = 260, 283, 335, 438 nm), ▼ = DSA-C6 (λ = 259, 283, 339, 451 nm), and ◀ = DSA-C7 (λ = 259, 283, 339, 451 nm).

measured the absorption spectra of solid films of the five compounds, alternatively, as can be seen in Figure 3. The peak positions of films and solutions of DSA-C1–DSA-C7 are summarized in Table S2 in the Supporting Information. We can see that peaks larger than $\lambda = 400$ nm in crystals are slightly red shifted compared to those in solution except for compound DSA-C4. We also measured the absorption spectra of the crystals by diffuse reflectance spectroscopy (see Figure S13 in the Supporting Information). The absorption edges of the different crystals are shifted pronouncedly opposite to those of the dilute solutions (see Table S3 in the Supporting Information). Thus, the variation of the onset of the absorption spectra suggests that there should exist dipolar coupling in the five crystals.

Figure 4 depicts the fluorescence decay curves of the five crystals (excited by a picosecond semiconductor laser at λ = 375 nm). The curve of DSA-C1 displays a mono-exponential decay and the curves of DSA-C3–DSA-C7 display a bi-exponential decay. The fitting details can be found in the Supporting Information. Table 1 summarizes the fitting parameters. We



ChemPubSoc

Figure 4. Fluorescence decay curves (detected at the peak wavelength of the PL spectra) of the 9,10-bis((4-*N*,*N*-dialkylamino)styryl) anthracene crystals (\blacksquare = DSA-C1, \blacklozenge = DSA-C3, \blacktriangle = DSA-C4, \blacktriangledown = DSA-C6, and \blacklozenge = DSA-C7), the instrumental response (\triangleleft = IRF) is given for comparison. The inset shows the enlarged curves at the beginning of the decay.

Table 1. Parameters of the fluorescence decay curves of the five crystals.						
Compound	λ [nm]	$ au_1$ [ns]	τ ₂ [ns]	<i>A</i> ₁	A ₂	$ au^{\scriptscriptstyle{[a]}}$ [ns]
DSA-C1	593	2.99		1		2.99
DSA-C3	565	1.16	2.67	0.5988	0.4012	1.50
DSA-C4	567	1.67	3.62	0.5644	0.4356	2.18
DSA-C6	580	1.18	2.79	0.4877	0.5123	1.68
DSA-C7	609	1.16	2.67	0.4268	0.5732	1.72
[a] The weighted-average lifetime was calculated by: $1/\tau = A_1/\tau_1 + A_2/\tau_2$.						

also measured the fluorescent lifetime of the five compounds in dilute solution. All dilute solutions show a rapid decay, which is beyond the response limit of our instrument, but one thing we are sure is that all the lifetimes of the dilute solutions are less than 0.2 ns. Thus, the weighted-average lifetimes of DSA-C1-DSA-C7 in crystals are much longer than those in dilute solution. This is one characteristic for excimer formation. In the inset of Figure 4, there exists delay time between the maximum of the decay curves of DSA-C1-DSA-C7 crystals and that of the instrumental response (IRF), and the shortest delay time is about 0.8 ns. The delay time corresponds to the dynamic formation of excited dimers, which is another characteristic of excimer formation. The above-mentioned two characteristics added by the structureless and red-shifted broadened spectra of the crystals indicate that the emission of the five crystals at least have the component of excimer emission, that is, emission from excitonic coupling.

Crystal structures

X-ray crystallographic analyses were performed to clarify the stacking patterns of the crystals. The results indicate that all the crystals of DSA-C1–DSA-C7 belong to the triclinic space group $P\overline{1}$ with one molecule per unit cell (Z=1, see Table S1 in the Supporting Information for the crystallographic data), and that the molecules in every crystal have the identical orientation. The polarization axes of all compounds are along the

long axis of the molecules according to the density functional theory (DFT) calculations by using the B3LYP hybrid functional with the 6-31G(d, p) basis set through Gaussian 09.^[46] That is, every molecular transition dipole is parallel to the others in each crystal.

To present the stacking patterns of the crystals clearly, we used a set of rules of color in the schematic diagram. For example, a partial illustration of the X-ray structure of DSA-C1 containing eight monomolecules is shown in Figure 5, the red \rightarrow pink is used to display the molecules along the *a* axis, red \rightarrow yellow to show the molecules along the *b* axis, red \rightarrow blue to show the molecules along the *c* axis. This set of rules of color presenting the molecules along different axes was extended to all crystals of DSA-C1–DSA-C7 in the following figures.



Figure 5. A diagram presenting the molecules along different axis by using different colors (red and pink, blue and pale blue, yellow and pale yellow).

In the single crystal of DSA-C1, the molecules are self-assembled together by three-dimensional, net-like supramolecular interactions. There exists aromatic C–H··· π bonds between benzene and anthracene. DSA-C1-I, -II, and -III present the aromatic C–H··· π bonds along the *a*, *b*, and *c* axis, respectively, as shown in Figure 6. The details of the intermolecular bonds are collected in Table 2.

In the single crystal of DSA-C3, the molecules are firstly selfassembled together by one aliphatic C–H··· π (DSA-C3-I) bond along the *a* axis, forming columns. Then the columns are selfassembled together in parallel along the *b* and *c* axes by the combination of van der Waals forces and steric hindrance effect, thereby forming the crystal. The procedure is shown in Figure 7. In the single crystal of DSA-C4, the molecules are selfassembled together in the same way as described for DSA-C3, only the reacting distance and angle of the C–H··· π bond are a little different, as can be seen from Table 2.

In the single crystal of DSA-C6, the molecules are firstly selfassembled into one plane (plane *ab*) by two-dimensional, netlike supramolecular interactions including three C–H··· π bonds. One is an aromatic C–H··· π (DSA-C6-I) bond, where the anthracene moiety donates an hydrogen atom and the benzene unit acts as the acceptor. The other two are aliphatic C–H··· π (DSA-C6-II and DSA-C6-III) bonds. Then the planes are pack together







Figure 6. Formation procedure of a DSA-C1 crystal. From the single molecule (a) to the three-dimensional, net-like stacking (e) by C–H··· π bonds along the *a* axis (b), C–H··· π bonds along the *b* axis (c), and C–H··· π bonds along the *c* axis (d).

Table 2. Parameters of the C–H… π bonds in the crystals.				
C—H…π bond	H…ring distance [Å]	C…ring distance [Å]	C—H…ring angle [°]	
DSA-C1-I	3.10	3.80	134	
DSA-C1-II	3.07	3.69	125	
DSA-C1-III	2.90	3.69	143	
DSA-C3-I	2.76	3.51	138	
DSA-C4-I	2.74	3.55	147	
DSA-C6-I	2.93	3.72	144	
DSA-C6-II	3.18	3.93	136	
DSA-C6-III	3.05	3.83	138	
DSA-C7-I	2.99	3.76	140	
DSA-C7-II	2.90	3.83	161	
DSA-C7-III	2.88	3.73	146	

in parallel along the *c* axis by the combination of van der Waals forces and steric hindrance effects, thereby forming the crystal. Figure 8 shows the procedure. In the single crystal of DSA-C7, the molecules are self-assembled together in the similar way of described for DSA-C6, see Figure S5 in the Supporting Information for the details of the three C–H··· π bonds. The distances and angles of the three C–H··· π bonds are slightly different from those in the DSA-C6 single crystal, see Table 2.

The crystal packing diagram with a unit cell and molecular conformation in the single crystals of DSA-C1–DSA-C7 can be found in the Supporting Information.

Discussion

The molecules of DSA-C1–DSA-C7 have the same arrangement (slipped-parallel arrangement) in the crystal structure, and only the slip angles and distances are different, which offers ideal experimental samples correlating the slip angle and distance with color.



Figure 7. Formation procedure of a DSA-C3 crystal. From the single molecule (a) to columns by $C-H\cdots\pi$ bonds along the *a* axis (b), and then the columns stack together (c), thereby forming the crystal.



Figure 8. Formation procedure of a DSA-C6 crystal. From the single molecule (a) to the layer overspread plane *ab* (b) by C–H··· π bonds (c), (c) is obtained by partially enlarging (b), and then the planes stack together along the *c* axis (d), thereby forming the crystal.

Chem. E	ur. J.	2014	<i>20.</i> 9991	- 9997

ChemPubSoc Europe



Curtis et al. defined the pitch and roll displacements to measure the π overlap between adjacent parallel molecules in crystals.^[47] The pitch and roll displacements are referred to the displacement between adjacent molecules relative to one another in the direction of the long molecular axis and the short molecular axis, respectively. The pitch and roll displacements and the distances between the adjacent molecules along different axes and in different planes for crystals of DSA-C1–DSA-C7 are shown in Table 3.

In order to choose the biggest π -overlap between adjacent molecules, the three parameters (pitch displacement, roll displacement, and distance) should be as small as possible. According to the above-described principle, the adjacent molecules along the *c* axis in the crystal of DSA-C1, along the *a* axis in the crystal of DSA-C4, in plane *ab* in the crystal of DSA-C6, and along the *b* axis in the crystal of DSA-C7 are chosen to investigate the dipolar coupling between them, as shown in Figure 9.

According to the dipolar coupling theory,^[30, 32] there is Equation (1):

$$\Delta E_{\rm di} \propto (1 - 3\cos 2\theta)/r^3 \tag{1}$$

 ΔE_{di} represents the energy difference between the excited state in the dimer and in the monomer, θ stands for the pitch angle, *r* is defined as the distance between the centroids of

Table 3. Pitch (x) displacement, roll (y) displacement, z displacement, and r for all neighboring molecules in crystals of DSA-C1–DSA-C7.					
Dimer	Pitch (x)	Roll (v)	z ^[a]	r ^[b]	
systems	displacement [Å]	displacement [Å]	displacement [Å]	[Å]	
DSA-C1					
along the <i>a</i> axis	7.33	2.36	5.40	9.11	
along the <i>b</i> axis	6.08	7.02	7.02	9.29	
along the <i>c</i> axis	8.02	1.29	5.09	9.51	
in plane <i>ac</i> ^[c]	15.36	3.65	4.21	15.93	
DSA-C3					
along the <i>a</i> axis	2.55	2.01	4.42	5.11	
along the <i>b</i> axis	5.38	7.13	7.44	9.19	
along the <i>c</i> axis	9.89	11.87	15.69	18.55	
DSA-C4					
along the <i>a</i> axis	2.66	2.40	4.62	5.34	
along the <i>b</i> axis	5.45	7.37	7.72	9.45	
along the c axis	15.16	5.81	11.81	19.21	
DSA-C6					
along the <i>a</i> axis	7.87	7.38	7.33	10.77	
along the <i>b</i> axis	1.49	10.22	10.87	10.97	
in plane <i>ab</i>	9.36	2.85	5.82	11.02	
along the c axis	6.90	0.36	9.56	11.79	
in space <i>abc</i>	16.26	3.20	5.81	17.27	
DSA-C7					
along the <i>a</i> axis	6.46	4.33	6.30	9.02	
along the <i>b</i> axis	9.20	0.77	4.81	10.38	
in plane <i>ab</i>	15.66	5.10	4.02	16.17	
along the <i>c</i> axis	0.67	14.14	14.95	14.96	

[a] The z displacement is determined by r and the pitch angle. [b] The value of r stands for the distance between the centroids of the chromophores in a dimer. [c] The plane ac represents the plane determined by the a axis and the c axis, as well as plane ab represents the plane determined by the a axis and the b axis. Space abc means the three-dimensional space determined by the a, b, and c axes.

the chromophores in the dimer. The values of θ and r can be found in Table 3.

The results of the absorption and emission spectra as well as of the fluorescent lifetime in solution and crystal of DSA-C1– DSA-C7 have shown that there exists both excitonic and dipolar couplings in crystals. So the total energy difference between the excited states in crystal and in dilute solution can be expressed as Equation (2):

$$\Delta E_{\text{total}} = \Delta E_{\text{di}} + \Delta E_{\text{ex}} = k \left(1 - 3\cos 2\theta \right) / r^3 + \Delta E_{\text{ex}}$$
(2)

 ΔE_{di} and ΔE_{ex} represent the energy difference between the excited state in the crystal and in dilute solution caused by the dipolar and excitonic couplings, respectively, k is the proportional coefficiency.

We calculated the values of $(1-3\cos 2\theta)/r^3$, as well as the values of the energy difference from the PL spectra of the crystals and the dilute solutions. Then we plotted the curve of the energy difference as a function of $(1-3\cos 2\theta)/r^3$ and fitted it by using Equation (2), as shown in Figure 10. The fitted Equation (3) is given below.

$$\Delta E_{\text{total}} = 38.53 \, (1 - 3\cos 2\theta) / r^3 - 0.074 \tag{3}$$

The correlation coefficient R^2 of the fitting is not very high (0.69). The difference of the torsion angles (the vinylene–an-

thryl torsion angle and vinylene-phenyl torsion angle) between the monomolecules and the crystals is small (see Table S4 in the Supporting Information), so we consider them as the minor factor affecting the optical properties of the crystals in this work, but it still has some effect. In additions, only when the roll displacements are zero, Equation (1) can be strictly obeyed, actually they are not zero (see Table 3). The above-mentioned two reasons induce the low R^2 value. However, from Equation (3), we still quantitatively obtained the contribution to the spectral shift from the dipolar and excitonic couplings, respectively. Here, the intercept is -0.074 eV, meaning that the spectra will be red shifted by 19 nm from $\lambda = 559$ nm (emission from the dilute solution) to $\lambda = 578$ nm (emission from the crystal) for DSA-C1 and by 20 nm from $\lambda =$ 564 nm (emission from the dilute solution) to $\lambda =$ 584 nm for DSA-C3–DSA-C7 (emission from the crystal) due to the excitonic coupling ($\Delta \lambda_{\text{excitonic}}$). The total spectral shift ($\Delta \lambda_{total}$) subtracted by 19 nm (DSA-C1) or 20 nm (DSA-C3-DSA-C7) is the contribution from the dipolar coupling ($\Delta \lambda_{dipolar}$ Table 4).

From Table 4 we can see that the dipolar coupling causes the blue-shifted spectra for the crystals of DSA-C3, DSA-C4, and DSA-C6 and the red-shifted spectra for the crystals of DSA-C1 and DSA-C7. This means that the crystals of DSA-C3 and DSA-C4 are H-aggregates, and the crystals of DSA-C1 and DSA-C7 are J-aggregates. For the crystal of DSA-C6, the spectral shift caused by dipolar coupling is only -3 nm, and the distance between the selected adjacent mol-

Chem. Eur. J. 2014, 20, 9991 – 9997





Figure 9. Dominant interactions, pitch angle between the adjacent molecules with the biggest π -overlap, and distance between the centroids of the neighbor chromophores in each crystal.

ecules is 5.82 Å, which is the biggest one in the five crystals. So the spectral shift induced by dipolar coupling can be neglected in the crystal of DSA-C6. The experiments of amplified spontaneous emission (ASE) have been performed for the five crystals. The results indicate that there is no ASE in crystals of DSA-C3, DSA-C4, and DSA-C6, whereas there exists ASE in the crystal of DSA-C1 (see Ref. [26]) and DSA-C7 (Figures S11 and S12 in the Supporting Information, respectively).



Figure 10. Energy difference ΔE (calculated from the peak position of the PL spectra of the crystals and the dilute solutions) as a function of $(1-3\cos 2\theta)/r^3$ (**n**). They can be linear fitted by using Equation (2), (solid line). The slope is 38.53, the intercept is -0.074, and R^2 is 0.69.

Table 4. Optical properties of the DSA series in solution and in the solid state (single crystals) at room temperature: emission (λ_{em}) wavelengths, spectral shift, and quantum yields (φ_{e}).

	DSA-C1	DSA-C3	DSA-C4	DSA-C6	DSA-C7
solution					
$\lambda_{\rm em}$ [nm]	559	564	564	564	564
solid state					
λ_{em} [nm]	594	565	567	581	609
$\Delta\lambda_{ ext{total}}$ [nm]	35	1	3	17	45
$\Delta \lambda_{\text{excitonic}}$ [nm]	19	20	20	20	20
$\Delta \lambda_{ ext{dipolar}}$ [nm]	16	-19	-17	-3	25
φ _F ^[a] [%]	59.4	29.2	21.2	43.8	52
[a] $\phi_{\rm F}$ is the PL efficiency of the crystals.					

According to the dipolar coupling theory,^[30,32] the interaction of the parallel transition dipoles will induce the excited state to split into two levels. For the J-aggregation, the lower-split level transition is allowed and the higher-split level transition is forbidden; for the H-aggregation, it is reversed, as shown in Figure S14 in the Supporting Information. So the crystals with J-aggregation have the high quantum efficiency, whereas the crystals with H-aggregation have the low quantum efficiency. This has been confirmed by the measurements of the quantum efficiency of the crystals (see Table 4). When the molecules are excited, electrons firstly jump into the higher-split level and then quickly relax into the lower-split level. Because the lowersplit level is relatively stable, electrons are gathered in it. Because the lower-split level transition is allowed for J-aggregation, the gathered electrons in the lower-split level induce the inversion, which is a necessary condition for ASE. That is why ASE is observed in crystals of DSA-C1 and DSA-C7.

Conclusion

Five 9,10-bis((4-*N*,*N*-dialkylamino)styryl) anthracene derivatives (DSA-C1–DSA-C7) with different length alkyl chains were synthesized. They showed the same color in dilute solutions but different colors in the crystal state. X-ray crystallographic analyses reveal that all the crystals of DSA-C1–DSA-C7 belong to the triclinic space group $P\bar{1}$ with one molecule per unit cell and

Chem. Eur. J	2014 , 20,	9991 – 9997
--------------	-------------------	-------------



A European Journal

the molecules in every crystal have the identical orientation. The results of the measurements of the optical properties in solution and in the crystal state of DSA-C1–DSA-C7 have shown that both excitonic and dipolar couplings exist in the crystals. For the first time, we studied the cooperation of excitonic and dipolar couplings between adjacent molecules in crystals in detail, and quantitatively obtained the contribution to the spectral shifts (emission from the monomolecule to the crystal) from the excitonic and dipolar couplings, respectively. Our results suggest that the excitonic and dipolar couplings are both important for the optical properties of organic crystals. The experiments of ASE and measurement of the quantum efficiency confirmed our finding, which will improve the understanding of structure–property relationships of crystals.

Acknowledgements

This work was supported by the National Science Foundation of China (grant numbers 61275036, 91233113, 21221063, and 51170092). The authors are grateful to Ling Ye (SKLSSM) for the X-ray diffraction experiments and to Bao Li (SKLSSM) for the direction on X-ray structural analyses.

Keywords: dipolar coupling • excitonic coupling • single crystals • stacking patterns • structure–property relationships

- M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, T. Koyama, Y. Taniguchi, Adv. Mater. 2003, 15, 213–217.
- [2] H. Yanagi, T. Ohara, T. Morikawa, Adv. Mater. 2001, 13, 1452-1455.
- [3] Y. Li, F. Shen, H. Wang, F. He, Z. Xie, H. Zhang, Z. Wang, L. Liu, F. Li, M. Hanif, L. Ye, Y. Ma, Chem. Mater. 2008, 20, 7312–7318.
- [4] A. L. Briseno, S. C. B. Mannsfeld, M. Ling, S. Liu, R. J. Tseng, C. Reese, M. Roberts, Y. Yang, F. Wudl, Z. Bao, *Nature* 2006, 444, 913–917.
- [5] V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* 2004, 303, 1644–1646.
- [6] H. Li, B. C. K. Tee, G. Giri, J. W. Chung, S. Y. Lee, Z. Bao, Adv. Mater. 2012, 24, 2588–2591.
- [7] H. Yu, Z. Bao, J. H. Oh, Adv. Funct. Mater. 2013, 23, 629-639.
- [8] H. Yanagi, T. Morikawa, S. Hotta, Appl. Phys. Lett. 2002, 81, 1512-1514.
- [9] X. Li, Y. Xu, F. Li, Y. Ma, Org. Electron. 2012, 13, 762-766.
- [10] R. J. Tseng, R. Chan, V. C. Tung, Y. Yang, Adv. Mater. 2008, 20, 435-438.
- [11] G. Chen, H. Sasabe, W. Lu, X.-F. Wang, J. Kido, Z. Hong, Y. Yang, J. Mater. Chem. C 2013, 1, 6547–6552.
- [12] G. Chen, H. Sasabe, Y. Sasaki, H. Katagiri, X.-F. Wang, T. Sano, Z. Hong, Y. Yang, J. Kido, *Chem. Mater.* **2014**, *26*, 1356–1364.
- [13] M. Cai, Z. Gao, X. Zhou, X. Wang, S. Chen, Y. Zhao, Y. Qian, N. Shi, B. Mi, L. Xie, W. Huang, *Phys. Chem. Chem. Phys.* **2012**, *14*, 5289–5296.
- [14] H. Y. Zhang, Z. L. Zhang, K. Q. Ye, J. Y. Zhang, Y. Wang, Adv. Mater. 2006, 18, 2369–2372.
- [15] B.-K. An, S.-K. Kwon, S.-D. Jung, S. Y. Park, J. Am. Chem. Soc. 2002, 124, 14410–14415.
- [16] J. Cornil, D. Beljonne, J. P. Calbert, J. L. Brédas, Adv. Mater. 2001, 13, 1053–1067.
- [17] J. He, B. Xu, F. Chen, H. Xia, K. Li, L. Ye, W. J. Tian, J. Phys. Chem. C 2009, 113, 9892–9899.
- [18] K. Kinashi, K.-P. Lee, S. Matsumoto, K. Ishida, Y. Ueda, Dyes Pigm. 2012, 92, 783-788.
- [19] C. Kitamura, Y. Abe, T. Ohara, A. Yoneda, T. Kawase, T. Kobayashi, H. Naito, T. Komatsu, *Chem. Eur. J.* **2010**, *16*, 890–898.
- [20] J. Mizuguchi, J. Phys. Chem. A 2000, 104, 1817-1821.

- [21] J. Mizuguchi, T. Senju, J. Phys. Chem. B 2006, 110, 19154-19161.
- [22] M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, A. Sironi, J. Am. Chem. Soc. 2000, 122, 5147–5157.
- [23] J. Cornil, D. A. dos Santos, X. Crispin, R. Silbey, J. L. Brédas, J. Am. Chem. Soc. 1998, 120, 1289–1299.
- [24] R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. P. Rath, N. Tamaoki, S. Das, J. Phys. Chem. C 2008, 112, 2137-2146.
- [25] S. Saito, K. Nakakura, S. Yamaguchi, Angew. Chem. 2012, 124, 738-741; Angew. Chem. Int. Ed. 2012, 51, 714-717.
- [26] Y. L. Wang, T. L. Liu, L. Y. Bu, J. F. Li, C. Yang, X. J. Li, Y. Tao, W. J. Yang, J. Phys. Chem. C 2012, 116, 15576–15583.
- [27] Z. Xie, B. Yang, F. Li, G. Cheng, L. Liu, G. Yang, H. Xu, L. Ye, M. Hanif, S. Liu, D. Ma, Y. Ma, J. Am. Chem. Soc. 2005, 127, 14152–14153.
- [28] B. Xu, H. Fang, Y. Dong, F. Chen, Q. Chen, H. Sun, W. Tian, New J. Chem. 2010, 34, 1838–1842.
- [29] T. Zhou, F. Li, Y. Fan, W. Song, X. Mu, H. Zhang, Y. Wang, Chem. Commun. 2009, 3199–3201.
- [30] P. W. Bohn, Annu. Rev. Phys. Chem. 1993, 44, 37-60.
- [31] D. Braga, F. Grepioni, L. Chelazzi, M. Campana, D. Confortini, G. C. Viscomi, CrystEngComm 2012, 14, 6404–6411.
- [32] M. Kasha, H. R. Rawls, M. A. EL-Bayoumi, Pure. Appl. Chem. 1965, 11, 371–392.
- [33] Y. Liao, B. E. Eichinger, K. A. Firestone, M. Haller, J. Luo, W. Kaminsky, J. B. Benedict, P. J. Reid, A. K. Y. Jen, L. R. Dalton, B. H. Robinson, *J. Am. Chem. Soc.* 2005, *127*, 2758–2766.
- [34] R. H. Rohrbaugh, P. C. Jurs, W. P. Ashman, E. G. Davis, J. H. Lewis, Chem. Res. Toxicol. 1988, 1, 123-127.
- [35] D. T. Stanton, P. C. Jurs, Anal. Chem. 1990, 62, 2323-2329.
- [36] L. Bu, M. Sun, D. Zhang, W. Liu, Y. Wang, M. Zheng, S. Xue, W. Yang, J. Mater. Chem. C 2013, 1, 2028.
- [37] L.-H. Xie, X.-Y. Hou, Y.-R. Hua, Y.-Q. Huang, B.-M. Zhao, F. Liu, B. Peng, W. Wei, Org. Lett. 2007, 9, 1619.
- [38] H. Li, G. Giri, J. B.-H. Tok, Z. Bao, MRS Bull. 2013, 38, 34-42.
- [39] Z. Zhang, D. Yao, T. Zhou, H. Zhang, Y. Wang, Chem. Commun. 2011, 47, 7782-7784.
- [40] N. S. S. Kumar, S. Varghese, N. P. Rath, S. Das, J. Phys. Chem. C 2008, 112, 8429–8437.
- [41] N. S. S. Kumar, S. Varghese, C. H. Suresh, N. P. Rath, S. Das, J. Phys. Chem. C 2009, 113, 11927 – 11935.
- [42] J. Gierschner, M. Ehni, H. J. Egelhaaf, B. Milian Medina, D. Beljonne, H. Benmansour, G. C. Bazan, J. Chem. Phys. 2005, 123, 144914.
- [43] S. K. Park, S. Varghese, J. H. Kim, S.-J. Yoon, O. K. Kwon, B.-K. An, J. Gierschner, S. Y. Park, J. Am. Chem. Soc. 2013, 135, 4757–4764.
- [44] S.-J. Yoon, S. Varghese, S. K. Park, R. Wannemacher, J. Gierschner, S. Y. Park, Adv. Opt. Mater. 2013, 1, 232.
- [45] P. F. van Hutten, V. V. Krasnikov, H. J. Brouwer, G. Hadziioannou, Chem. Phys. 1999, 241, 139–154.
- [46] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Krnox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, C. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Onnenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [47] M. D. Curtis, J. Cao, J. W. Kampf, J. Am. Chem. Soc. 2004, 126, 4318– 4328.

Received: February 26, 2014 Published online on July 10, 2014

Chem. Eur. J. 2014, 20, 9991 – 9997

www.chemeurj.org

9997