Exciton Properties of Organic Molecules Revealed by Inelastic X-ray Scattering

Organic optical materials attract much attention because of their important applications in light emitting devices, biosensors, and nonlinear optical devices among many others [1]. As the optical processes are largely dominated by excitonic excitations in these materials, it would greatly benefit the material design if one knew the location of excitons in molecules, and how the movement of an exciton is correlated with the local structure. To study these properties, one needs momentum resolved information. For the first time, we have performed inelastic X-ray scattering (IXS) on an organic molecular crystal using beamline **BL12XU** [2]. IXS is one of most powerful experimental method for investigating electronic excitations. Unlike conventional techniques such as absorption and Raman scattering, IXS can provide both energy and momentum resolved information. Moreover, unlike electron energy loss spectroscopy, IXS can work well in the high q region. These advantages are crucial for studying exciton behavior in organic molecules with complex local structures. The present target material is the open-ring photomerocyanine form of spirooxazines (Py-SO, $C_{21}N_4O_2H_{22}$). One unit cell of the Py-SO crystal is shown in Fig. 1.

Figure 2(a) shows the IXS data with momentum transfer q along the a axis. After Raleigh background subtraction, three distinct features were found around 2.2 eV (I), 4.6 eV (II) and 6.6 eV (III) as shown in Figs. 2(b) and 2(c). A weak feature II' also can be observed in Fig. 2(c). The spectral features are identified as the optically excited singlet excitons (I, II, II') and interband transitions (III). Based on the ZINDO/SCI method [3,4], the calculated IXS spectra are shown in Fig. 2(d) for a molecular aggregate of a six-unit-cell stack with the shortest intermolecular separations. There is almost a one-to-one correspondence between the experimental features I-III and theoretical

features A-C. The energy centroid positions of features B, B' and C coincide with those of features II, II' and III, respectively. Both feature C and D involve many excitations. Correspondingly, the spectra in the experiment exhibit a very broad feature III followed by rising spectral weight. The experimental feature I disperses from 2.2 eV to 2.07 eV. This is well reproduced in the theoretical spectra, except that the calculated position is about 0.48 eV higher. The small exciton dispersion reflects the weak intermolecular coupling. In the aggregate calculation, the strongest intermolecular coupling is estimated to be 55 meV. Therefore, the excitons are still Frenkel excitons that are confined mostly in a single molecule. As a result, single molecule excitations could be computed to study the local distribution of the electrons and holes. Figure 2(e) shows the IXS spectra calculated for molecular excitations of a single Py-SO molecule, where energy levels of excited states are indicated by straight lines. As expected, the spectra are very similar to the aggregate calculations. The energy gap between LUMO and HOMO is calculated to be 5.62 eV, denoted by the dashed line. Moreover, calculation shows that feature A corresponds to a discrete exciton. Feature B contain mostly two excitons, and features C and D are made up of tens of excitations above the gap. For further confirmation, IXS spectra were also measured for momentum transfer perpendicular to the a direction in the ac plane, which also shows good agreement with the theoretical calculation. The fact that the theoretical calculation based on a single molecule shows good agreement with the experimental data indicates that the exciton distribution within the molecule is well captured as a result of the weak coupling between the molecules.

Figures 3(a) – 3(e) are exciton wave functions presented in a way that the false color scale indicates the possibility P(x, y) for finding an electron at atom site x and a hole at atom site y. The gray scale of the solid circles in the inset shows the possibility P(x) = Σ_yP(x, y) of finding the electron or hole at site x on the Py-SO molecule. For feature A, the exciton is mostly situated in the middle region. For feature B, on the other hand, both of the two main excitons are extended over the entire molecule and are much larger than the lowest energy exciton (Figs. 3(e) and 3(f)). For comparison, the two main inter-gap excitations of feature III are shown in Figs. 3(g) and 3(h): one is considerably localized in the phenyl ring; the other is extended.
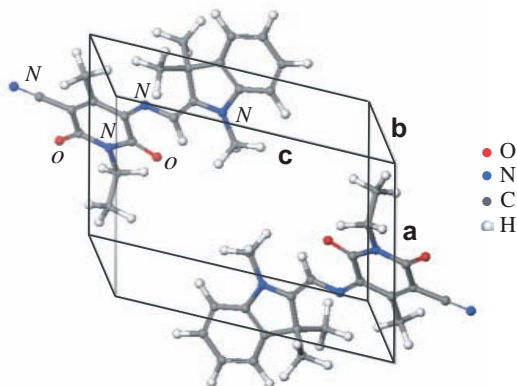
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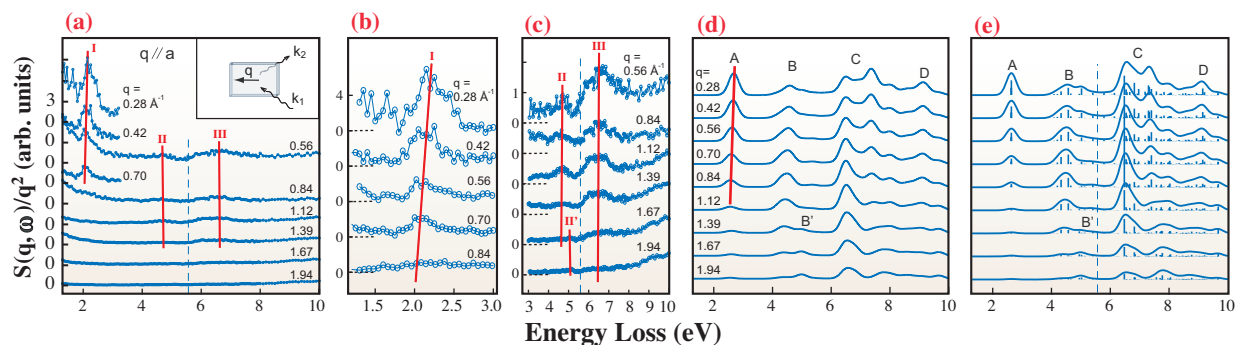

Fig. 1. A unit cell of a Py-SO molecular crystal.

Fig. 2. **(a)** IXS data of Py-SO with q along the a axis. The spectral intensities are divided by q^2. **(b)**, **(c)** enlargements of spectra shown in **(a)** with the elastic line removed. ZINDO/SCI simulated spectra for q along the a axis based on **(d)** the aggregate and **(e)** a single molecule. The dashed lines in panels **(a)**, **(c)**, and **(e)** indicate the calculated HOMO-LUMO gap energy.

organic molecular crystal for the first time. The experimental results are free of multiple scatterings and therefore can be directly compared with theory. The dispersion of the exciton is retrieved from IXS for the first time and gives a good measure of the strength of intermolecular coupling. Combined with suitable quantum chemical calculations, reliable and comprehensive properties of excitons can be obtained, which are crucial for understanding their optical properties and for designing materials of desired optical properties based on exciton transfer or dissociation properties.
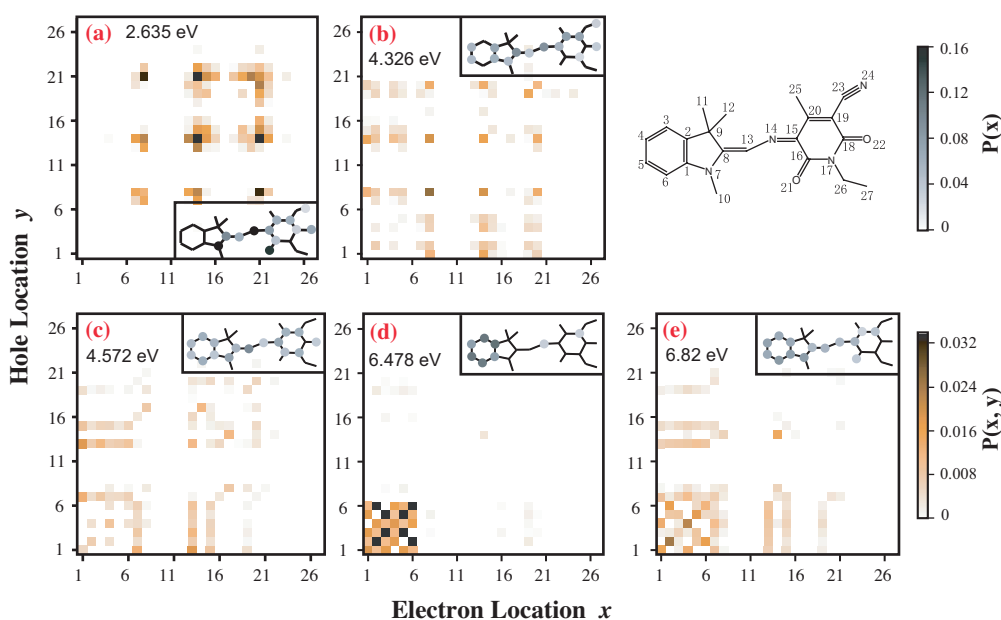

Fig. 3. False color plots for the calculated possibility P(x,y) for **(a)** the lowest energy exciton; **(b, c)** two main excitations of feature B; **(d, e)** two main excitations of feature C. The atom sites are numbered in the top right corner. The atoms plotted in gray scale in the inset represent P(x).

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