Real-space Investigation of Energy Transfer with Single-molecule Luminescence and Absorption Spectroscopy

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ABSTRACT

Single-molecule absorption spectroscopy with ultimate spatial resolution and sensitivity was developed by using a localized surface plasmon at the tip of a scanning tunneling microscope to overcome the diffraction limit. We also report on the molecular-level investigation of energy transfers in an atomically well-defined heterogeneous molecular dimer by the combination of single-molecule absorption spectroscopy with the scanning tunneling luminescence technique.

INTRODUCTION

Exciting the electronic states of molecules leads to various important energy conversion processes, such as luminescence, photochemical reactions, and photovoltaic systems. Thus, detailed understanding of the electronically excited states of molecules is crucial to improve and develop organic energy conversion devices based on opto-electronic and/or chemical processes. A scanning tunneling microscope (STM) combined with optical illumination/detection systems is an ideal tool for investigating such energy dynamics of a single molecule on the solid surfaces. Here we report on the development of single-molecule absorption spectroscopy [1] with unprecedented sensitivity and spatial resolution, in which a localized plasmon at the tip apex of the STM tip is utilized as an electrically-driven excitation source with sub-atomic precision, on the basis of a photon-STM that we have developed [2].

Absorption spectroscopy is a powerful tool to observe excited molecular states; its combination with emission spectroscopy that deals with deexcitation processes is effective in investigating the energy dynamics at excited molecular states. Single-molecule luminescence detection has recently shown rapid progress and become indispensable in various research fields, such as quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, single-molecule absorption spectroscopy has been developing relatively slowly due to an intrinsic problem regarding the light source that excites target molecules. A difficulty lies in the difference between the diffraction limit of excitation light and the absorption cross section of a single molecule. It has been known that the localized surface plasmon (LSP), a collective electromagnetic field spatially confined around a metal nanostructure, is generated near the STM tip surface below the diffraction limit when bias voltage is applied. The generated localized electric field has been extensively utilized for near-field optical spectroscopies, high-efficiency solar cell devices and photocatalysis. By using the interaction between LSP and a molecular exciton, we realized single-molecule absorption spectroscopy, which further is combined with single-molecule luminescence spectroscopy to investigate energy transfer between two different molecules [3].

DEVELOPMENT OF A SINGLE-MOLECULE ABSORPTION SPECTROSCOPY

Scanning tunneling luminescence (STL) spectroscopy, where luminescence is induced by the injection of electrons from the STM tip, provides a unique tool for investigating optical properties of solid surfaces with atomic scale precision [1-16]. A previous STL experimental
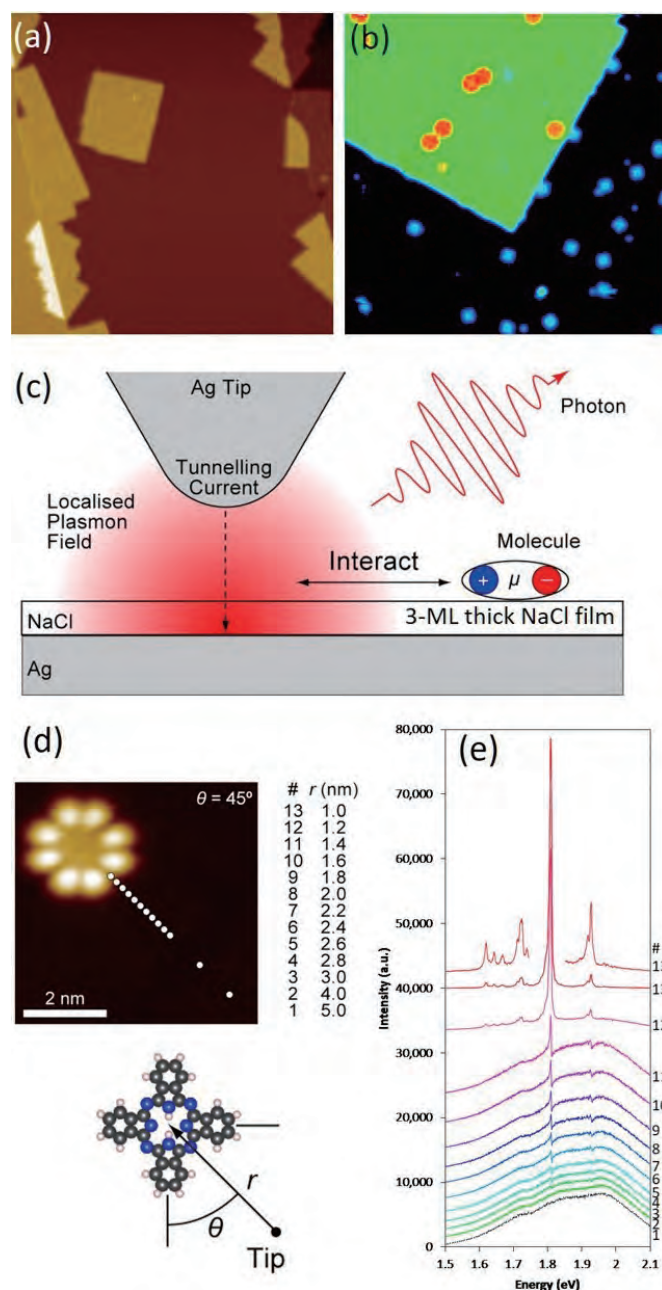
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Fig. 1: STM images of (a) a 3-ML thick NaCl film on the surface of Ag(111) surface (150 × 150 nm²) (b) H$_2$Pc molecules on the surface (40 × 40 nm²). The scanning conditions for STM imaging were Vs (sample bias-voltage) = -2.5 V and It (tunneling current) = 2 pA. (c) A schematic diagram illustrating the experiment. (d) The lateral tip positions from the center of a H$_2$Pc molecule for the spectra measurements as shown in (e) and the definition of the coordinates around the molecule.

study reported that part of the energy of the LSP generated by the tip is absorbed by the molecules nearby the STM tip [17,18], which implies that the electronic excitation of the molecule by the LSP, not by the direct electron injection, can be achieved in the STM configu-

ration. Theoretical investigations pointed out that the LSP-molecule interactions leading to the energy transfer processes, such as emission and absorption, and interference effects can significantly modify the spectral shape of a molecular luminescence spectrum [19-21]. These pioneering works showed a possible way to utilize the LSP-molecule interaction to near-field excitation of a single molecule, which enabled us to establish single-molecule absorption spectroscopy.

Fig. 1(a) shows a topographic image of a three-monolayer (3 ML) thick NaCl film grown on an Ag(111) single crystal surface. A low-temperature STM (Scienta Omicron Inc.) combined with photon detection units was used to carry out all experiments at 5 K under ultrahigh vacuum. The ultrathin NaCl film decouples the molecular orbitals from the metallic substrate so as to prevent electronic quenching of the excited molecule, which enables optical investigation with the photon-STM [7]. The free-base phthalocyanine (H$_2$Pc) molecules were deposited on to the surface as shown in Fig. 1(b).

Fig. 1(c) illustrates the design of the experiment to precisely investigate the near-field interaction between an LSP and a molecular exciton. The tunneling current of the STM generates the LSP that then interacts with the molecule, and the photons emitted from this coupled system are detected. The strength of the LSP-exciton coupling is finely tuned by changing the lateral distance between the molecule and the location of the LSP with angstrom precision (Fig. 1(d)). We also define the coordinates around the molecule. A series of luminescence spectra by application of a tunneling current was obtained near H$_2$Pc/NaCl as a function of the lateral distance of the STM tip from the center of the molecule as shown in Fig. 2(e). When the tip is placed far from the molecule (r ≥4 nm, # 1, 2), the luminescence spectrum is dominated by a broad emission, which is attributed to the radiative decay of the LSP. Remarkably, two dip structures emerge at 1.81 and 1.92 eV in the broad spectrum when the tip is positioned close to the molecule (r = 1.4–3 nm, # 3–11), and the spectral features becomes prominent as the tip is closer to the molecule. When the STM tip reaches the edge of the molecule, where direct excitation of the molecule by carrier injection from the tip turns into a possibility, intensive molecular luminescence is observed (# 12,13). The luminescence peaks at 1.81 and 1.92 eV are attributed to transitions from the first and second singlet excited states of H$_2$Pc, known as the Q$_x$ and the Q$_y$ states [22,23], respectively.
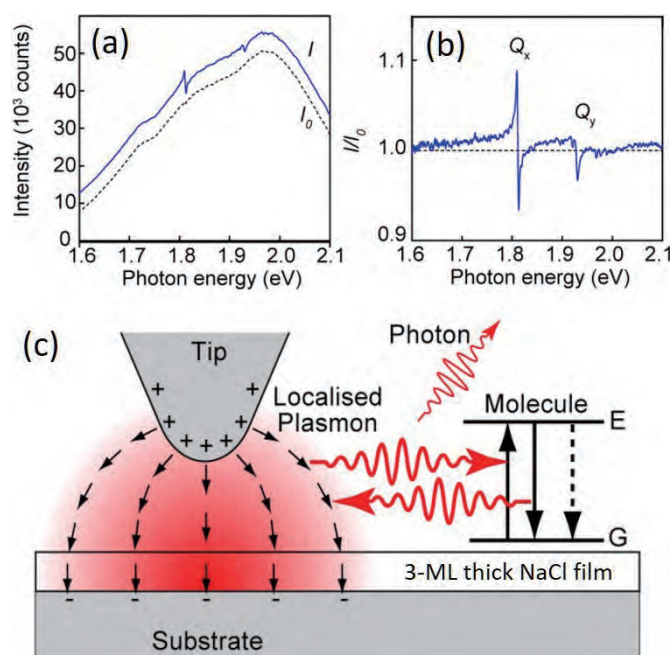
Fig. 2: (a) STL spectra measured at r = 2.2 nm (upper, blue solid line) and 4 nm (lower, black dotted line) (θ = 45°, V = -2.5 V, I = 250 pA, t = 5 min). (b) An I(r, θ)/I0 spectrum (r = 2.2 nm, θ = 45°), generated by dividing the upper curve (I) with the lower curve (I_0) in (a). (c) A schematic diagram illustrating the dynamic processes resulting from the plasmon-exciton coupling. G and E stand for the ground and excited states of the molecule, respectively. The energy of the LSP is absorbed by the molecule (upward arrow), and then the energy is re-emitted into LSPs (downward solid arrow) or the energy is non-radiatively dissipated (downward dashed arrow).

Fig. 2(a) shows two representative STL spectra measured with tip positions far from and close to the molecule. We define the STL spectrum measured with the tip located far from the molecule as the excitation source spectrum I0, and that measured close to the molecule as I(r, θ). As shown in Fig. 2(b), the ratio spectrum I/I$_0$ clearly reveals the change in the spectral shape resulting from the plasmon-exciton coupling. The larger dip at 1.81 eV corresponding to the Q_x state has an asymmetric feature, and the smaller dip at 1.92 eV corresponding to the Q_y state has a more complex shape.

The energy of LSP is absorbed by the molecule, and then the energy of the excited molecule is re-emitted into the LSP. These processes interfere with each other, and the constructive and destructive interference of these processes leads to enhancement and suppression of the energy transfer, resulting in asymmetric spectral shapes [20,21]. These dynamic processes in the coupled plasmon-exciton system are schematically summarized in Fig. 2(c).

REAL-SPACE INVESTIGATION OF ENERGY TRANSFER BETWEEN MOLECULES

Energy transfer is an essential dynamic process in naturally configured photosynthetic systems [24-27], and it has also been used in various artificially designed energy-harvesting devices [28-30]. Diverse functions have been realized by different regulations of the energy dynamics, and researchers have been pursuing the microscopic understanding and molecular-level control of energy transfers, envisaging the creation of novel functionalities. So far, optical spectroscopy has been widely used to investigate excitation dynamics and many interesting features of energy transfers among coupled molecules have been unveiled [25-27]. However, the spatial resolution of conventional optical spectroscopy is limited to a few 100 nm, and the details of energy transfer on the nanoscale is still largely unknown. Here we show a molecular-level investigation of energy transfers in atomically well-defined heterogeneous molecular dimers consisting of a H_2Pc and magnesium phthalocyanine (MgPc) by single-molecule absorption and luminescence spectroscopy using the STM [1].
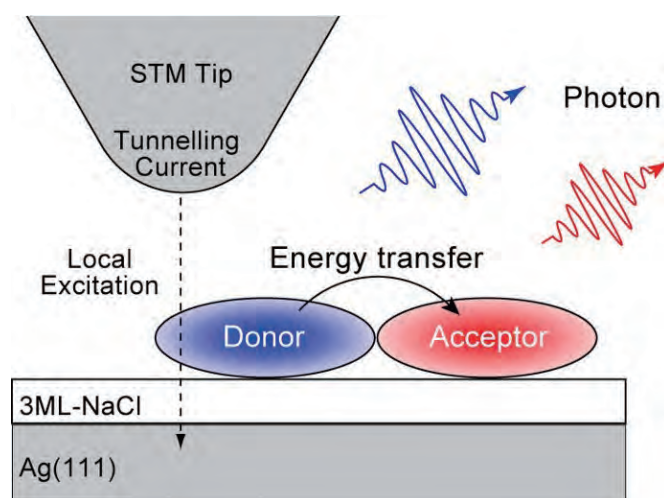

Fig. 3: A schematic diagram describing the experiment to investigate energy transfer between two different molecules.

Fig. 3 depicts our experimental setup to investigate energy transfers between donor and acceptor molecules. The atomically confined tunneling current of STM excites only the donor molecule, and the photons emitted from this coupled molecular system are detected. MgPc and H_2Pc were selected as donor and acceptor, respectively, because they show fluorescence at significantly different energies [31].
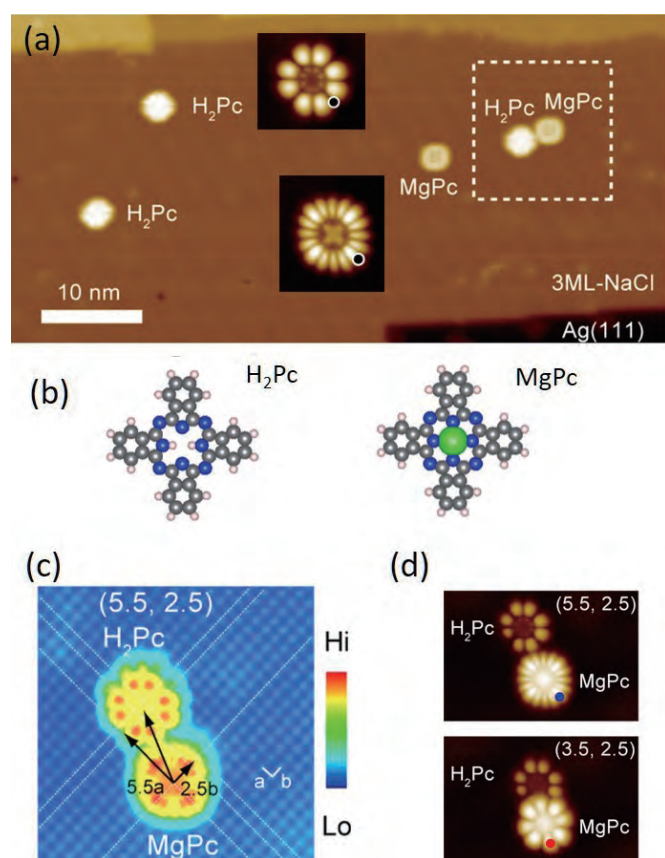
Fig. 4: (a) An STM image of H_2Pc and MgPc molecules on a 3ML-thick NaCl film grown on Ag(111) ($V_s = 1$ V, $I_t = 5$ pA). (b) Structural models of both molecules (grey: C, blue: N, white: H, green: Mg). (c) An STM image of a H_2Pc-MgPc dimer measured with a CO-terminated tip (V = -2.5 V, $I_t = 2$ pA). Dimer configurations are specified with a vector connecting the molecular centers of H_2Pc and MgPc, where the unit vectors, α and β, are between the nearest neighbor chlorines. (d) STM images of dimers measured with an Ag tip (V = -2.3 V, $I_t = 5$ pA). Comparing the upper (5.5, 2.5) dimer to the bottom (3.5, 2.5) dimer images, H_2Pc was moved to change the dimer configuration.

Fig. 4(a) shows the topographic STM image of the sample, where MgPc, H_2Pc, and CO molecules are co-deposited on an ultrathin NaCl film grown on Ag(111). Inset images represent high-resolution STM images of a single H_2Pc (upper) and MgPc (lower) molecules. The adsorption structures of MgPc and H_2Pc on the NaCl film were determined with atomic precision using a CO-terminated STM tip [32,33] (Fig. 4(c)). Briefly, the center of H_2Pc adsorbs on a sodium ion with the molecular axes aligned in the [010] or [001] directions, whereas the center of MgPc adsorbs on a chlorine ion with the molecular axes tilted $\pm 38°$ from the [010] or [001] directions. The peculiar 16-lobe appearance of an isolated MgPc molecule is formed by the rapid shuttling motion between the two equivalently stable adsorption angles ($+38° \leftrightarrow -38°$) [34]. Two different dimers with (5.5, 2.5) and (3.5, 2.5)

configurations were investigated. Notably, the shuttling motion of MgPc is stopped in the (3.5, 2.5) configuration because the two angles $\pm 38°$ are no longer equivalent, resulting in the typical eight-lobe appearance for many phthalocyanines [35].

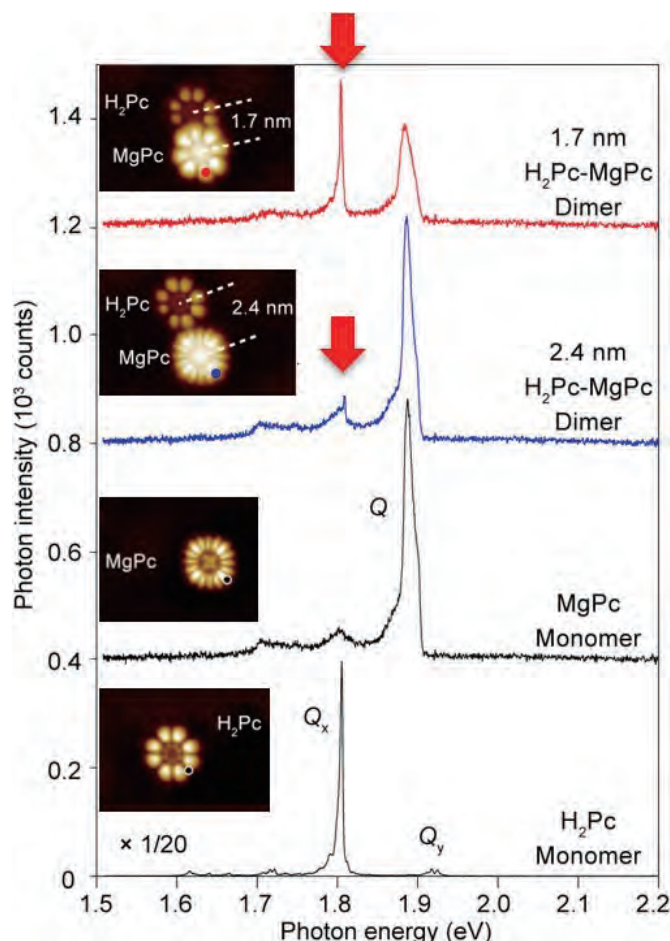**Fig. 5:** STL spectra of a H_2Pc monomer, a MgPc monomer, (5.5, 2.5) dimer, and (3.5, 2.5) dimer. The red and blue curves were measured at the red and blue points in d. The measurement conditions for H_2Pc monomer were V = -3 V, It = 30 pA, and exposure time t = 1 min, and those for others were V = -1 V, It = 30 pA, and t = 1 min.

Fig. 5 Shows the STL spectra obtained with the STM tip placed over the MgPc in the two MgPc-H_2Pc dimers and the STL spectra of MgPc and H_2Pc monomers as references. The MgPc monomer shows a fluorescence peak from the S1 state (Q state) at 1.89 eV. Due to the symmetry of a H_2Pc molecule possessing two hydrogen atoms in the center of the molecule, the Q state, which is doubly degenerate in many four-fold symmetric phthalo-cyanines, splits into two excited states, Q_x and Q_y [1,22]. Hence, the H_2Pc monomer shows a sharp and intense fluorescence peak from the S1 state (Q_x) at 1.81 eV

and a weak fluorescence from S2 (Q_y) at 1.92 eV [1]. In the (5.5, 2.5) dimer with an intermolecular distance of 2.4 nm, a sharp fluorescence peak of H_2Pc at 1.81 eV was observed while locally exciting the MgPc. The peak of H-2Pc Q_x fluorescence became pronounced in the (3.5, 2.5) configuration with a shorter intermolecular distance of 1.7 nm. The intensity increases of H_2Pc fluorescence accompanied a decrease of MgPc Q fluorescence, clearly indicating energy transfer from MgPc to H_2Pc.
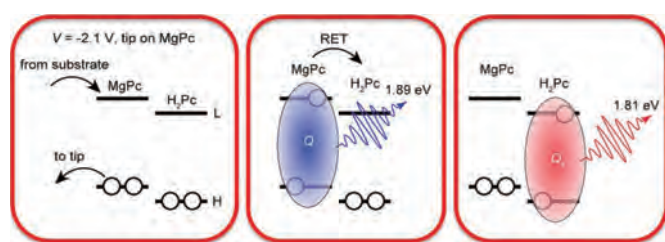

Fig. 6: Schematic illustrating the dynamic process for the energy transfer. It was assumed that the STM was above MgPc.

Figure 6 shows the carrier and energy dynamics in the MgPc-H_2Pc dimer induced by the hole injection into the highest occupied molecular orbital (HOMO) of MgPc [12]. The injected hole into the HOMO of MgPc remains there, because the hole transfer to H_2Pc is blocked by the energy barrier at the MgPc-H_2Pc junction. The hole in the HOMO of MgPc is most probably filled with electron transfer from the metal substrate. However, there is a non-negligible probability of electron supply to the lowest unoccupied molecular orbital (LUMO) of MgPc from the metal substrate, leading to exciton formation in MgPc. This is rrationalized by the reduction of the electron-injection barrier into the LUMO, which is induced by hole injection into the HOMO and the potential drop in the NaCl film. Once the Q state is formed in MgPc, energy transfer by charge transfer (CT) is again prohibited by the energy barrier. The Q state of MgPc (1.89 eV) is higher in energy than the Q_x state (1.81 eV) of H_2Pc, but lower than the Q_y state (1.92 eV) of H_2Pc; therefore, the only allowed mechanism for energy transfer is resonance energy transfer (RET) from the Q state of MgPc to the Q_x state of H_2Pc.

The spectral overlap of the fluorescence of MgPc and the absorption of H_2Pc was examined to reveal RET pathways (Fig. 7(a)). Single molecule absorption spectra of H_2Pc reveal the electronic transitions polarized in the
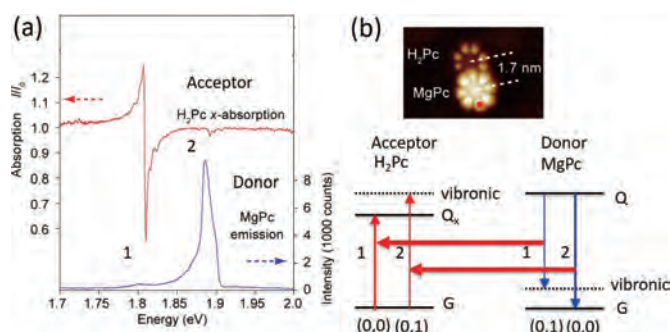

Fig. 7: (a) Spectral overlap of MgPc emission (blue) and H_2Pc absorptions (red). (b) An STM image showing the (3.5, 2.5) dimer and schematic illustration of the two main RET pathways.

x-direction (x-absorption) and those polarized in the y-direction (y-absorption). In addition to the strong features at 1.81 eV in x and at 1.92 eV in y, vibronic satellites of each transition are clearly seen in the higher energy sides. Two RET pathways (1) from Q to the vibrationally excited state of Q_x, and (2) from Q to the vibrational ground state of Q_x, which accompanies a vibronic excitation in MgPc, are evidenced.

CONCLUSION

In this work, we demonstrate that the ability of LSP to focus light near the STM tip far beyond the diffraction limit can be applied to realize single-molecule absorption spectroscopy. Our works further provides an atomic-scale real-space view of dynamic quantum state transition in donor-acceptor molecular systems, which was achieved by the combination of local excitation by a scanning tunneling microscope and precise spectroscopic analysis of the excited luminescence from the coupled molecular system. Our novel ways of inducing resonance energy transfer and controlling its flow could pave the way to realize ultrafast excitonic circuits with molecular architectures.

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