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Dark states enhance the photocell power *via* phononic dissipation

Yiteng Zhang,[a] Aaron Wirthwein,[b] Fahhad H. Alharbi,[c] Gregory S. Engel[d] and Sabre Kais*[ce]

The high efficiency of the photon-to-charge conversion process found in photosynthetic complexes has inspired researchers to explore a new route for designing artificial photovoltaic materials. Quantum coherence can provide a mean to surpass the Shockley–Quiesser device concept limit by reducing the radiative recombination. Taking inspiration from these new discoveries, we consider a linearly-aligned system as a light-harvesting antennae composed of two-level optical emitters coupled with each other by dipole–dipole interactions. Our simulations show that the certain dark states can enhance the power with the aid of intra-band phononic dissipation. Due to cooperative effects, the output power will be improved when incorporating more emitters in the linear system.

I. Introduction

It is well known that the photon-to-charge quantum conversion efficiency of photosynthesis in plants, bacteria, and algae can be almost 100% under certain conditions.[1–9] Under the condition of 100% quantum efficiency, according to Shockley and Quiesser, the efficiency of photovoltaic energy conversion is limited to about 33% by the radiative recombination of electron–hole pairs, thermalization, and unabsorbed photons.[10,11] Of all the causes, radiative recombination was believed to be unavoidable due to two-level system population dynamics.[12] However, Scully *et al.* suggested that it is possible to take advantage of coherence generated by an external driving field to supress recombination by altering the dynamics and hence detailed balance – the principle in which radiative recombination is rooted.[13,14,19–23] Subsequently, reduced radiative recombination was observed experimentally in quantum well solar cells.[15]

Recently, it has been shown that certain dark states induced by dipole–dipole interactions – an internal source of coherence – can slow exciton recombination, leading to considerable power conversion enhancements.[9,16] In this work, the donors – antennae that absorb incident solar photons – and the acceptor are intentionally organized in order to increase the efficiency of the photocell model. However, as the number of donors increases, it will become more and more complex, even impossible, to achieve the required molecular orbitals. One of the common molecular aggregates with dipole–dipole interactions is the H-aggregate. Basically, the H-aggregate is a series of linearly-aligned molecules, so to explore the possibility of designing a solar cell using H-aggregation here we study the properties of linearly-aligned two-level optical emitters. In such a system, certain dark states can work as ratchets to extract photons since phononic dissipation will preferentially mediate transition into these dark states, where optical decay cannot occur if the energy separation between the intra-band dark and bright states falls into the vibrational spectrum of the absorbing antennae.[17] Starting from the linearly-aligned-donor model, we also propose a toy model for circularly aligned donors and the acceptor can extract excitons from all the donors with the same extraction rate.

Therefore, we propose two solar cell models with the configurations shown in Fig. 1. The light-harvesting systems are composed of two-level optical emitters aligned both linearly and circularly. We will show that in these models, phononic dissipation combined with certain dark states can enhance photocell efficiency.

II. Model

In our model, the Hamiltonian governing the linear antennae system H_ℓ can be described as (assuming $\hbar = 1$ for convenience)

$$H_\ell = \omega\sum_{i=1}^{N}\sigma_i^+\sigma_i^- + J\sum_{i=1}^{N-1}(\sigma_i^+\sigma_{i+1}^- + \text{h.c.}), \qquad (1)$$

where ω is the bare transition energy of each emitter, J is the dipole–dipole interaction constant between nearest pairs, and $\sigma_i^\pm$ denote the raising and lowering operators which create and

[a] Department of Physics, Purdue University, West Lafayette, IN, 47907, USA
[b] Department of Physics, Wabash College, Crawfordsville, IN, 47933, USA
[c] Qatar Environment and Energy Research Institute, HBKU, Doha, Qatar
[d] Department of Chemistry, Institute for Biophysical Dynamics, and The James Franck Institute, University of Chicago, Chicago, IL, 60637, USA
[e] Department of Chemistry, Department of Physics and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA. E-mail: kais@purdue.edu

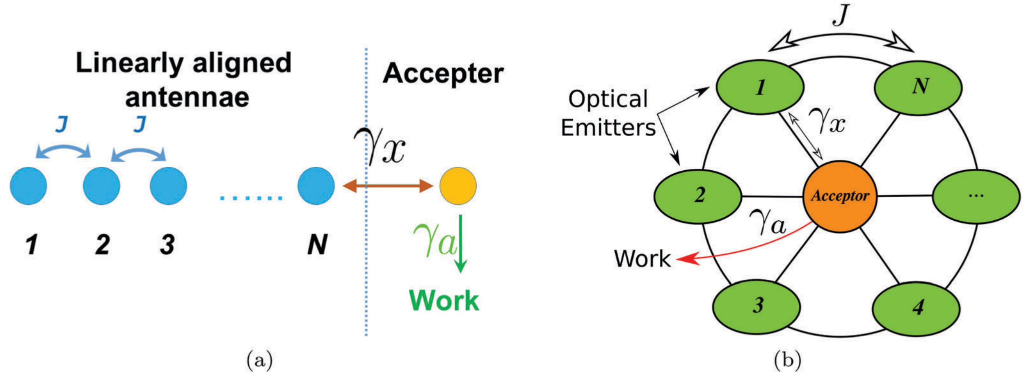

Fig. 1 Scheme of the solar cell models composed of (a) linearly- and (b) circularly-aligned photon absorbing antennae attached to an acceptor. The nearest-neighbor pairs are coupled with each other *via* dipole–dipole interactions, indicated by the constant J. The acceptor can only extract excitons from the donor at the end of the system in the linear model, whereas in the circular model, extraction occurs from each emitter in the antennae system. The hopping rate between the donor and the acceptor is γ_x and the excitons at the acceptor site are extracted to do work with a rate of γ_a.

destroy an exciton on the sites. The Hamiltonian for the circular system H_c has the following similar form:

$$H_c = \omega \sum_{i=1}^{N} \sigma_i{}^{+}\sigma_i{}^{-} + J \sum_{i=1}^{N} (\sigma_i{}^{+}\sigma_{i+1}{}^{-} + \text{h.c.}), \tag{2}$$

with the stipulation that $\sigma_{N+1}{}^{\pm} = \sigma_1{}^{\pm}$, which describes the closed-ring arrangement sketched in Fig. 1b. After diagonalization, the Hamiltonian of the antennae systems can be rewritten as

$$H_{\ell/c} = \sum_K \lambda_K |K\rangle\langle K|,$$

where $|K\rangle$ describes the eigenstate with eigenenergy λ_K. The eigenstates of $|K\rangle$ can be categorized into several energy bands based on the number of excitons. The rate of optical transitions connecting eigenstates with one exciton difference is proportional to

$$\Gamma_{KK'} = |\langle K'|J_+|K\rangle|^2,$$

where $J_\pm = \sum_i^N \sigma_i{}^{\pm}$.

Certain eigenstates of the system can work as ratchets to amplify the absorption with zero emission. Consider the first energy band of a four-emitter linear system as an example. There are totally four states in this band with energies $\omega \pm \frac{1}{2}(\sqrt{5} \pm 1)J$. The ground state can only be excited into the optical bright states with energies $\omega - \frac{1}{2}(\sqrt{5} - 1)J$ and $\omega + \frac{1}{2}(1 + \sqrt{5})J$ in this energy band. The other two are called dark states since the optical transition rate, proportional to $\Gamma_{KK'}$, is zero. Consequently, the dark states do not have pathways decaying back to the ground state. However, the bright states can decay to the dark states *via* phononic transitions and the dark states can then be further excited to the states in the second band. Therefore, the dark states in the band work like exciton ratchets, called ratchet states.[17] As for the circularly-aligned-donor system, the ratchet states have been well explained in ref. 17. It seems that the circularly-aligned-donor system has more ratchet states than the linearly-aligned-donor system.

Taking into account the light field *via* the standard light-matter-interaction Hamiltonian, the dissipater for the coupling of the system can be described as[17,18]

$$\begin{aligned} D_o[\rho_s] = \gamma_o \sum_{\omega_\Omega > 0} \Gamma_{KK'} \Big[(N(\omega_\Omega) + 1)\mathcal{L}\big[\hat{L}_\Omega^\dagger, \rho_s\big] \\ + N(\omega_\Omega)\mathcal{L}\big[\hat{L}_\Omega, \rho_s\big]\Big], \end{aligned} \tag{3}$$

where ρ_s is the density operator of the linear/circular system, γ_o is the decay rate of a single emitter, $\hat{L}_\Omega = |K\rangle\langle K'|$, and $N(\omega_\Omega) = \frac{1}{e^{\omega_\Omega k_B T} - 1}$ is the thermal occupancy of the optical mode with frequency ω_Ω. The sum in eqn (3) includes all optical modes with non-zero frequencies, *i.e.* $\omega_\Omega = \lambda_K - \lambda_K > 0$. And $[\hat{L},\rho]$ is the Lindbladian dissipater:

$$\mathcal{L}[\hat{L}, \rho] = \hat{L}\rho\hat{L}^\dagger - \frac{1}{2}\{\hat{L}^\dagger\hat{L}, \rho\}.$$

The collective inter-band transitions are described by the dissipater given in eqn (3).

The phononic transitions to certain dark states play a very important role in enhancing the efficiency. These types of transitions are caused by the interaction between states of the antennae system and the local bath of phonons.[17] Such interactions can be described as

$$H_{\ell/c-p} = \sum_q \sum_i^N g_q \sigma_i^z \left(\hat{a}_q + \hat{a}_q^\dagger\right), \tag{4}$$

where $\hat{a}_q(\hat{a}^\dagger)$ is the annihilation (creation) operator for the phonons of wavevector q with energy of ω_q and exciton–phonon coupling g_q. This interaction can only intermediate transitions within the same energy band since it commutes with $\sum \sigma_i^z$. Denote $|K_l^\nu\rangle$ and $|K_l^\mu\rangle$ as the eigenstates of $H_{\ell/c}$ with energies of $\lambda_K^{l\nu}$ and $\lambda_K^{l\mu}$, respectively, from the same energy band l. Thus, the intra-band transition operators $\hat{L}_p$ can be described as

$$\hat{L}_{\rm p}(l,\nu,\mu) = |K_l^\nu\rangle\langle K_l^\mu|.$$

Therefore, the dissipater due to interactions with the phonon bath can be written as

$$D_{\rm p}[\rho_{\rm s}] = \gamma_{\rm p} \sum_{l,\nu,\mu} \sum_{\omega_q>0} \left[(N(\omega_q)+1)\mathcal{L}[\hat{L}_{\rm p}(l,\nu,\mu)^\dagger, \rho_{\rm s}] + N(\omega_q)\mathcal{L}[\hat{L}_{\rm p}(l,\nu,\mu),\rho_{\rm s}] \right], \tag{5}$$

where $\omega_q = \Delta\lambda(l,\nu,\mu) = \lambda_K^{l\nu} - \lambda_K^{l\mu}$ is the intra-band energy gap. The summation over ω_q includes all positive frequencies. As known, the rate of phonon relaxation $\gamma_{\rm p}$ is usually much faster than optical transition rate. We can set $\gamma_{\rm p}$ as 1000 times $\gamma_{\rm o}$, *i.e.* $\gamma_{\rm p} = 1000\gamma_{\rm o}$. This setup of timescales allows population to leave the bright states before reemission.[17]

To form a complete photovoltaic circuit, we include an acceptor A, with excited state $|\alpha\rangle$ and ground state $|\beta\rangle$, which connects to the antennae system. Emitters connected to the acceptor are called donors. The acceptor acts as a "work load" to convert the energy of excitons into electrical power. The Hamiltonian governing the acceptor is

$$H_{\rm A} = \omega_{\rm A}\sigma_{\rm A}{}^+\sigma_{\rm A}{}^-, \tag{6}$$

where $\omega_{\rm A}$ is the transition frequency of the acceptor, and $\sigma_{\rm A}{}^+ = |\alpha\rangle\langle\beta|(\sigma_{\rm A}{}^- = |\beta\rangle\langle\alpha|)$ is the raising (lowering) operator. Here we set the acceptor frequency $\omega_{\rm A}$ to be resonant with the frequency of our emitters ω, *i.e.* $\omega_{\rm A} = \omega$.

For general cases, the extraction of excitons from donor to acceptor could simply be an incoherent hopping process. Thus, the extraction mechanism from the linear system can be described as

$$D_{x\ell}[\rho] = \gamma_x \mathcal{L}[\sigma_{\rm N}{}^-\sigma_{\rm A}{}^+, \rho], \tag{7}$$

while the extraction from the circular system can be written as

$$D_{\rm xc}[\rho] = \gamma_{\rm x} \sum_{i=1}^{N} \mathcal{L}[\sigma_i{}^-\sigma_{\rm A}{}^+, \rho], \tag{8}$$

where ρ is the joint density matrix combining the respective antennae system and the acceptor. That is, $\rho = \rho_{\ell/c} \otimes \rho_{\rm A}$ where $\rho_{\rm A}$ is the density matrix for the acceptor.

Integrating all the aforementioned dissipation and decay processes, the master equation governing the dynamics of the density matrix is obtained:

$$\dot{\rho} = -i[H_{(\ell/c){\rm A}},\rho] - D_{\rm o}[\rho] - D_{\rm p}[\rho] - D_{{\rm x}(\ell/c)}[\rho] - D_{\rm A}[\rho], \tag{9}$$

where $H_{(\ell/c){\rm A}} = H_{\ell/c} \oplus H_{\rm A}$ and $D_{\rm A}[\rho] = \gamma_{\rm a}\mathcal{L}[\sigma_{\rm A}{}^-, \rho]$ is the decay process of the acceptor with decay rate $\gamma_{\rm a}$.

Now we incorporate the theory of Quantum Heat Engines[14] to evaluate the current and voltage of the proposed model as a solar cell. The current can be evaluated *via* the formula

$$I = e\gamma_{\rm a}\langle\rho_\alpha\rangle_{\rm ss}, \tag{10}$$

where e is the fundamental charge of the electron and $\langle\rho_\alpha\rangle_{\rm ss}$ is the steady state population of the acceptor's excited state. The decay rate $\gamma_{\rm a}$ depends on the nature of the acceptor, which can be considered a "load" resistance. The cell voltage driving the "load" to work can be described as

$$eV = \hbar\omega_{\rm A} + k_{\rm B}T_{\rm p}\ln\left(\frac{\langle\rho_\alpha\rangle_{\rm ss}}{\langle\rho_\beta\rangle_{\rm ss}}\right) \tag{11}$$

where $k_{\rm B}$ is the Boltzmann's constant and $T_{\rm p}$ is the temperature of the phonon bath, which we set at room temperature so that $T_{\rm p} = 300$ K.

III. Results

In order to study the relationship between voltage and current as well as power, we varied the decay rate $\gamma_{\rm a}$ on the site of the acceptor to calculate $\langle\rho_\alpha\rangle_{\rm ss}$ and $\langle\rho_\beta\rangle_{\rm ss}$, the populations of the excited and ground states of the acceptor respectively. Other typical parameters are listed in Table 1. The results are shown in Fig. 2–6. A trivial feature is that when $\gamma_{\rm a} \to 0$, the work current will tend to zero, since $\gamma_{\rm a} = 0$ means that the "load" resistance is infinite, indicating the cell circuit has become an open circuit.

However, there is a very intriguing characteristic regarding phononic dissipation in the results shown in Fig. 2 and 3. The cell current and power will be much greater with phononic dissipation than without this kind of dissipation. Obviously, the maximum cell power is enhanced by phononic dissipation. According to our results, the maximum power and current are

Table 1 The parameters used in numerical calculations ($\hbar$ = 1). The parameters are equivalent to those used in ref. 17

Parameters	Symbols	Values (eV)
Emitter (acceptor) frequency	ω ($\omega_{\rm A}$)	1.80–2J
Dipole coupling constant	J	0.02
Optical decay rate	$\gamma_{\rm o}$	10^{-6}
Phononic decay rate	$\gamma_{\rm p}$	$1000\gamma_{\rm o}$
Extraction rate	$\gamma_{\rm x}$	$0.1\gamma_{\rm o}$

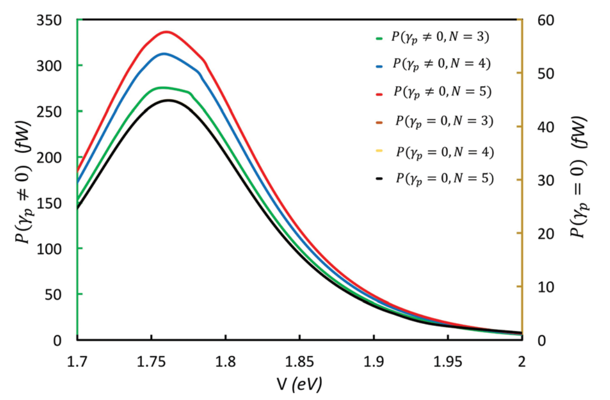

Fig. 2 The cell power as a function of voltage for N = 3, N = 4 and N = 5. The powers with and without phononic dissipation in the system use different scales. The powers without phononic dissipation almost overlap with each other for all three systems. The phononic dissipation can enhance the cell power greatly.

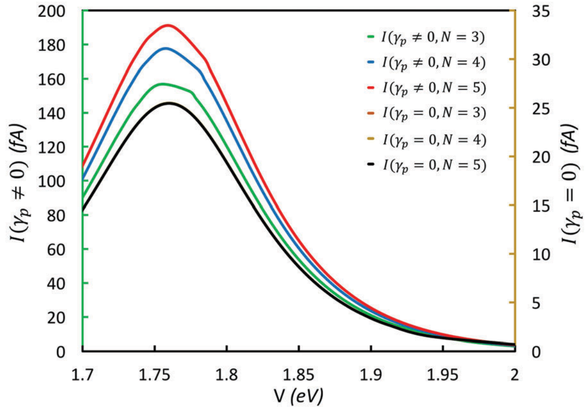

Fig. 3 The cell current as a function of voltage for $N = 3$, $N = 4$ and $N = 5$. The currents with and without phononic dissipation in the system use different scales. The currents without phononic dissipation almost overlap with each other for all three systems. Phononic dissipation can enhance the cell current greatly.

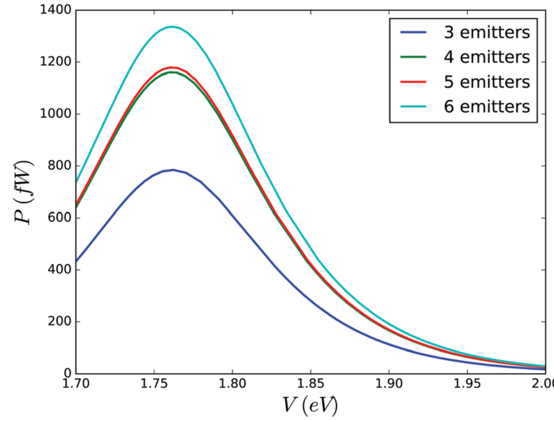

Fig. 5 A comparison of photocell power as a function of voltage for three-, four-, five-, and six-emitter systems in the circular configuration. Here we see greater enhancements that those of the linear model, with the exception of the four-to-five emitter enhancement.

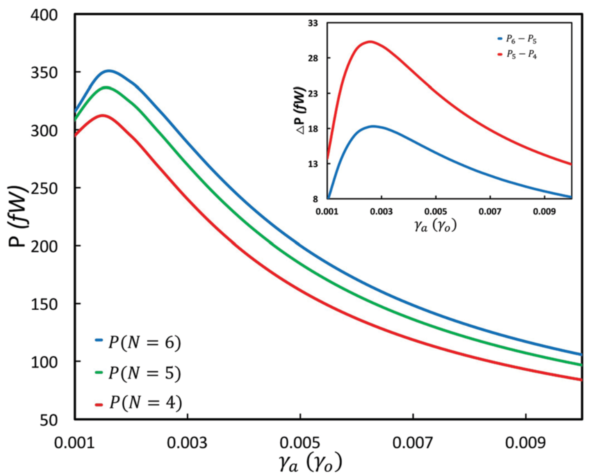

Fig. 4 The comparison of cell power as a function of γ_a for four-, five- and six-emitter systems. The embedded figure is the relationship between the differences of the cell power and the values of γ_a. The embedded figure shows the cell power differences as a function of γ_a. The red line in the embedded figure indicates the power difference between systems with five emitters and four emitters, $P_5 - P_4$ and the blue line for $P_6 - P_5$.

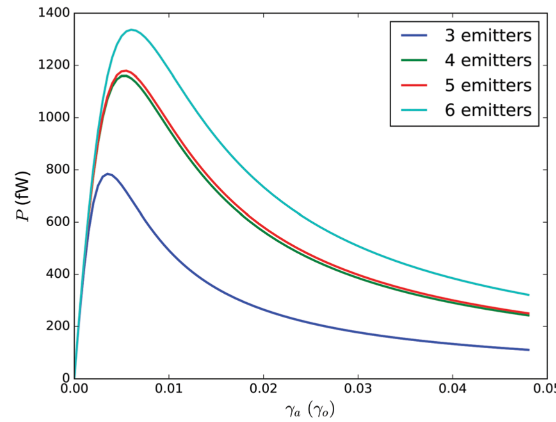

Fig. 6 A comparison of photocell power as a function of γ_a for three-, four-, five-, and six-emitter systems in the circular configuration. Notice the peak powers occurs around γ_a equal to $0.004\gamma_o$ to $0.008\gamma_o$.

enhanced about 6 times by phononic intra-band dissipation. Phononic dissipation can extract excitons from the bright states and transfer them to dark states. However, the channel for excitons to decay from dark states to the ground state is closed and excitons on the dark states can still be excited to upper levels. The joint effects greatly increase the populations of excitons at the site of acceptor. Therefore, the phononic intra-band dissipation makes the dark states work as ratchets to pull excitons from the ground state to excited states. As a result, these ratchet states can greatly enhance the cell power and current *via* phononic dissipation.

Having discussed the enhancing effect of phononic dissipation, we move on to explore the relationship between cell power and the number of emitters in the antennae systems. Intuitively, increasing the number of emitters in the linear model could decrease the populations on the acceptor site, since the acceptor can only extract excitons from the site of the end emitter connecting to it. Thus, the cell current and power would decrease when increasing emitters in a linearly-aligned system due to the decreased exciton population on the acceptor site. However, our simulations tell a different story from intuition. As shown in Fig. 2 and 3, without phononic dissipation, the output powers and currents almost overlap with each other for all three systems, indicating that the dilution effect of increasing the number of emitters is not obvious. However, the enhancement effect of increased ratchet states is outstanding, comparing the output powers and currents with phononic dissipation for these three systems.

Furthermore, the cell powers of four-, five- and six-emitter systems as a function of γ_a are compared, as shown in Fig. 4. The results show that the cell power is larger with more emitters in the system. According to the results, the maximum cell power of a five-emitter system is enhanced about ~7% compared to that of a four-emitter system and around ~4% for a six-emitter system compared to a five-emitter system. Such enhancements are likely caused by more ratchet states since an antennae system with more emitters will have more ratchet states. Again, this demonstrates that ratchet states are able to enhance the cell power.

In a word, the counterintuitive enhancements of cell current and power are mainly due to the effects of ratchet states. The enhancing effect of ratchet states neutralizes the dilution effect due to the increased emitter sites. However, the enhancing effect with more emitters will decrease as emitters increase, as shown in the embedded figure of Fig. 4. The percent enhancement caused by adding one emitter to a system with four emitters is larger than by adding one emitter to a system with five emitters. There must be a balance between the enhancing effect caused by the ratchet states and the dilution effect. This suggests the existence of an optimal number of emitters in the antennae systems to achieve the best efficiency in our proposed photocell model.

As for the circular model, we expected to circumvent the struggle between enhancement through ratchet states and the diminishing effects of dilution since while there are more emitters, there is also more extraction, increasing the population on the acceptor excited state. The results in Fig. 5 and 6 indicate this is not the case and we still must consider a balance between dilution and ratcheting effects for the circular model. The result do, however, show that given the same parameters, an *N*-emitter circular system out-performs the *N*-emitter linear system. This is likely due to the greater number of ratchet states and increased exciton extraction by the acceptor.

IV. Conclusion

In both the linear and circular arrangements of dipole-coupled molecules, the coherence caused by the dipole–dipole interaction induces dark states. Intra-band phononic dissipation enables these dark states to work as ratchets to extract excitons without decay, thereby breaking detailed balance. All these collective effects lead to enhanced cell current and power. The most intriguing result is that increasing emitters in the antennae can enhance the peak power. Such an enhancing effect might not always be true when the emitters exceed a certain number, but it is true at least when the number of emitters is not large. Both models have elucidated that a careful balance between dilution and ratcheting effects must be considered to achieve optimal photocell efficiency.

Unlike specially-arranged systems requiring specific molecular orbitals,[9,16] our proposed linear model is much easier to realize in practice. H-aggregates have been demonstrated to be capable of serving as light-harvesting antennae.[24] The property of H-aggregates to align in a parallel way and couple *via* dipole–dipole interactions make it a candidate device to implement our proposed linear photocell model.

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