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Spin-dependent recombination and electroluminescence quantum yield in conjugated polymers

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We study the mixing of singlet and triplet excitons due to spin-orbital coupling in conjugated polymers with ring twist angle θ. The mixing, proportional to $\sin^2\theta$, determines the singlet-triplet transition rates and the spin-dependent recombination of injected electrons and holes in the electroluminescence (EL) process. It is found that the EL quantum yield can in principle be higher than 1/4 if the exchange energy is either (1) so small that the back transition from triplet to singlet is faster than the triplet decay, or (2) so large that the lowest triplet exciton formation is slowed down by phonon bottleneck. In addition to large θ and small effective exciton-phonon coupling, heavy atom impurities can also increase the yield by enhancing the mixing.

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The development of light emitting diodes and displays based on conjugated polymers is now growing at a dramatic speed.[1] However, there remain many fundamental questions regarding both the electronic structure and device operation principles. Those questions must be clarified in order to fully understand the complex physical processes that eventually lead to light emission. One of the outstanding issues in this field regards the internal electroluminescence (EL) quantum efficiency η_{int}, defined as the number of photons generated per injected electron-hole pair. We can express η_{int} as $\gamma\eta_s q$, where γ is the exciton formation ratio per injected pair, η_s is the recombination branching ratio through the spin singlet,[2] and q is the singlet exciton radiative decay probability. As suggested by the photoluminescence (PL) in solution, q can be close to 1, while γ is improved by using multilayer structures[1]. Therefore, η_s can be taken as the intrinsic yield that sets the theoretical limit for η_{int}. η_s is considered to be 1/4 based on spin statistics.[1] This sets an upper bound on η_{int} at 1/4, much lower than the EL quantum yield achieved in inorganic semiconductors,[3] and poses a serious constraint for the development of highly efficient light emitting polymer devices. Recently Cao *et al.* compared the PL and EL quantum yields and suggested that η_s can be as large as 0.5.[4] We show in this work that the upper bound can be well above 1/4 when singlet-triplet transitions (intersystem crossing, or ISC) during the recombination process are taken into account, implying that there is still plenty of room for the improvement of efficiency in practice.

In this article, mixing through spin-orbital coupling and the resulting transition between singlet and triplet excitons in poly(phenylene-vinylene) (PPV) are studied. We find it crucial[5] to include an alternate twist of angle $\theta=5°-10°$ between benzene rings in the solid state.[6] Due to mixing, the triplet excitons can transfer to the singlet before they recombine. The transition lifetime τ_{ts} is long in conjugated polymers because the singlet exciton is higher in energy than the triplet by $\Delta=2J$, where J is the exchange energy. Δ has been estimated to be a few tenths of an eV.[1] However, this lifetime is to be compared with the triplet lifetime τ_{tg} which can be as long as a millisecond.[7] When τ_{ts} is comparable to or smaller than τ_{tg}, a fraction of the triplet excitons are not lost through nonradiative decay or phosphorescence but are transferred to the singlet and contribute to the EL yield, ultimately raising r_s above 1/4. However, if Δ is large enough to render $\tau_{ts}\gg\tau_{tg}$, this effect disappears and the recombination becomes spin independent with $\eta_s=1/4$. The exact magnitude of Δ has not been determined experimentally,[8] and is therefore taken as a variable in this work. It is predicted to be about 0.6 eV from model calculations.[9] But uncertainty remains because the result for the singlet energy is about 0.5–0.8 eV higher than the experimental values, partly due to the neglect of three-dimensional dielectric screening. The result 2.2 eV for the triplet is believed to be more reliable because the electron and hole are more tightly bound than in a singlet state, and should have a smaller size dependence and dielectric screening. If we identify the PL emission peak energy of 2.4 eV as the singlet exciton energy, the Δ is only 0.2 eV. On the other hand, a much larger value ($\Delta=0.9$ eV) is obtained from an *ab initio* calculation.[10]

Interestingly, there is another effect that increases the yield again at a large exchange energy: the phonon bottleneck effect. Once a loose bound state is formed, the electron-hole pair with given total spin relaxes through various excited states via cascade phonon emission toward tightly bound exciton states.[11] With the initial singlet-triplet ratio 1:3, the spin usually does not change during the fast subpicosecond process.[12] However, with a large exchange energy it becomes possible that the energy gap between the lowest (T_1) and the second lowest (T_2) triplet exciton bands is larger than the optical phonon energy. When this happens, a significant fraction of the T_2 states will make an intersystem crossing to become singlet (S) instead of staying in the triplet sector and relaxing to T_1 all together. In other words, the triplet relaxation channel is strangled at this bottleneck, and the higher triplet excitations are redirected to the singlet sector and contribute to the EL yield and raise η_s above 1/4. Triplet-triplet fusion to the singlet exciton has been identified as another way to increase the yield at high exciton densities.[7] This process is not effective, however, since the spin statistics predicts that only 1/9 of the triplet pairs are in the singlet configuration.[7] Even when the fusion does occur, half of the 3/4 excitation energy in the triplet sector is still lost because two triplet excitons produce only one singlet. In this work we focus on the yield at the low concentration limit and neglect fusion or any other exciton-exciton interactions. Spin-dependent recombination was recently studied as a single quantum transition with no energy relaxation.[13] We take a different approach and follow the theory on the capture processes in inorganic semiconductors which considers exciton formation as a cascade phonon emission process in which the energy of the electron-hole pair successively descends from the continuum to the bound states.[11] The ISC causes spin relaxation in addition to energy relaxation. Considering the large exciton binding energy, we believe our approach is more suitable for the capture and recombination processes. Below we first calculate the singlet-triplet mixing due to the spin-orbital coupling in a chain, and then insert the result into rate equations to determine the EL yield.

The tight-binding Bloch state of the π electrons in PPV is $\psi_{k,\lambda}(\vec{r})=\Sigma_n e^{ikna}\phi_{\lambda,k}(\vec{r}-\vec{R_n})$ where $\lambda=1,\ldots,8$ is the band index, and $\vec{R}_n=n\vec{a}$ labels the position of the repeat unit. $\vec{a}$ is the periodic vector and $a=|\vec{a}|$ is the lattice constant. The integer n is the repeat unit index. $\phi_{\lambda,k}(\vec{r})=\Sigma_{m=1}^{8}c_m^{\lambda}(k)\phi_{210}(\vec{r}-\vec{r}_m)$, where $\phi_{210}(\vec{r})$ is the carbon $2p_z$ orbital. The atomic label m within one unit is shown in the inset in Fig. 2 below. The coefficient $c_m^{\lambda}(k)$ and the energy band $\varepsilon_{\lambda}(k)$ are determined by diagonalizing the 8×8 tight-binding matrix.[14] The hopping integrals used are $t=2.4$ eV, $t_1=1.9$ eV, and $t_2=2.9$ eV for phenyl, single, and double bonds, respectively.[15] The lower four bands are filled while the upper four are empty in the ground state. We shall focus on the conduction band (lowest empty band) and the valence band (highest filled band) for the description of an exciton state. An exciton is a superposition of electron-hole pair states $|k_e s_e, k_h s_h\rangle$, where $k_{e(h)}$ and $s_{e(h)}$ are the momentum and spin for the electron (hole), respectively. The triplet exciton $|T\rangle$ is lower in energy than the singlet $|S\rangle$ by $\Delta\equiv E_S-E_T>0$. The total momentum of both excitons is fixed at zero. The excitons are expanded as[16] $|T(-1)\rangle=\Sigma_{k_e,k_h}T_{k_e,k_h}|k_e\downarrow,k_h\uparrow\rangle$, $|T(0)=\Sigma_{k_e,k_h}T_{k_e,k_h}(|k_e\uparrow,k_h\uparrow\rangle-|k_e\downarrow,k_h\downarrow\rangle)$, $|T(1)\rangle=\Sigma_{k_e,k_h}T_{k_e,k_h}|k_e\uparrow,k_h\downarrow\rangle$, and $|S\rangle=\Sigma_{k_e,k_h}S_{k_e,k_h}(|k_e\uparrow,k_h\uparrow\rangle+|k_e\downarrow,k_h\downarrow\rangle)$. $0,\pm1$ are the magnetic quantum numbers. The wave functions can be approximated by Lorentzians with $T_{k_e,k_h}=\delta_{k_e,k_h}\,(1/\sqrt{L})\,2\Delta_T^{3/2}/(k_e^2+\Delta_T^2)$ and $S_{k_e,k_h}=\delta_{k_e,k_h}(1/\sqrt{L})2\Delta_S^{3/2}/(k_e^2+\Delta_S^2)$, corresponding to exponential functions in real space. L is the chain length.

Now we include the spin-orbital interaction $\hat{H}_{so}=(-e/m^2c^2)\vec{S}\cdot\vec{p}\times\vec{\nabla}U(\vec{r})$, where $\vec{S}$ is the spin operator, $\vec{p}$ is the momentum operator, and $U(\vec{r})$ is the periodic pseudopotential for the carbon valence electrons. The spin-flipping matrix element $\langle\phi_{210}(\vec{r}),\uparrow(\downarrow)|\hat{H}_{so}|\phi_{210}(\vec{r}-\vec{r}_m),\downarrow(\uparrow)\rangle$ between wave functions at neighboring carbon sites equals zero unless the alternating twist of the benzene planes is taken into account. Two pairs (between atoms 6 and 7 and between atoms 8 and 1) in each unit cell experience the twist. The matrix representation of the total Hamiltonian H_0+H_{so} in the basis consisting of one singlet and three triplets defined above becomes

$$\begin{pmatrix} E_T & 0 & 0 & -A \\ 0 & E_T & 0 & 0 \\ 0 & 0 & E_T & A \\ -A & 0 & A & E_S \end{pmatrix}.$$

In practice we take $U(\vec{r})$ as the Coulomb potential with effective atomic number $Z=4$, and the off-diagonal term

$$\begin{aligned} A &\equiv \langle T(-1)|\hat{H}_{so}|S\rangle \\ &= -\Sigma_{k_e,k_h}T_{k_e,k_h}S_{k_e,k_h}[\langle k_h\downarrow|\hat{H}_{so}|k_h\uparrow\rangle \\ &\quad -\langle k_e\downarrow|\hat{H}_{so}|k_e\uparrow\rangle]. \end{aligned}$$

Since the conduction and valence band edges occur at $k=\pi/a$, the term inside the square brackets can be approximated at this k value. Using $c_m^{\lambda}(\pi a)$ and the explicit form of $\phi_{210}(\vec{r})$, A can be obtained as an analytical function of Δ_T and Δ_S. For $\Delta_T=1/(5a)$, $\Delta_S=1/(10a)$,[17] and $a=6.54$ Å, we get $A=0.023\sin\theta$ eV where θ denotes the twisting angle. The new eigenvalues and corresponding eigenfunctions are found to be

$$E_S+\frac{2A^2}{\Delta}\rightarrow|S\rangle-\frac{\sqrt{2}A}{\Delta}\frac{1}{\sqrt{2}}[|T(-1)\rangle-|T(1)\rangle],$$

$$E_T\rightarrow|T(0)\rangle \text{ and } \frac{1}{\sqrt{2}}[|T(-1)\rangle+|T(1)\rangle], \tag{1}$$

$$E_T-\frac{2A^2}{\Delta}\rightarrow\frac{\sqrt{2}A}{\Delta}|S\rangle+\frac{1}{\sqrt{2}}[|T(-1)\rangle-|T(1)\rangle].$$

Note that $|S\rangle$ mixes with only one of the three triplet states with amplitude $\sqrt{2}A/\Delta$. The ISC transition rate $1/\tau_{st1}$ from singlet to triplet exciton, made possible by the mixing, can be approximated by $(\sqrt{2}A/\Delta)^2(1/\tau)$ where $\tau=0.2$ ps is the energy relaxation time within the spin singlet sector. τ_{st1} enters the rate equation for the spin-dependent recombination discussed below.

The exciton formation can be divided into two stages. First the electron and hole capture each other to form a loose bond. Second, the bound state relaxes in both energy and spin. We believe that there is no spin dependence for the capture cross section in the first stage, because the exchange energy matters only when the electron and hole exist in the same unit cell.[16] The ratio between the numbers of loose singlet and triplet excitons is therefore 1:3. The deviation from this ratio happens only in the second stage, where the relevant transitions and their lifetimes are defined in Fig. 1. Assuming first that Δ is small and there is no phonon bottleneck effect, $1/\tau_{t2s}$ can be neglected in comparison with

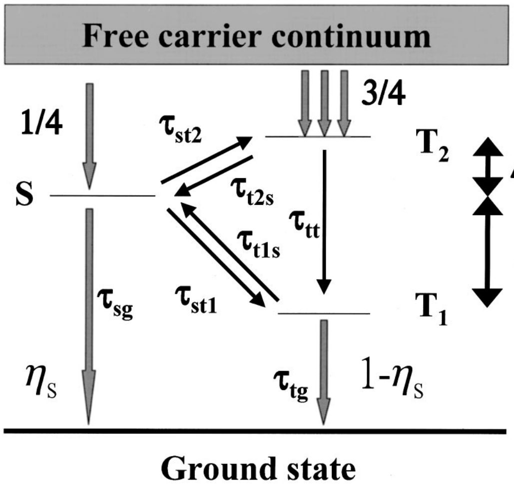

FIG. 1. The relevant transitions are shown with their transition lifetimes. S and T_2 excitons come from the continuum with ratio 1:3. After the possible intertransitions, all excitons must recombine through either the τ_{sg} or the τ_{tg} channel. The intrinsic yield η_s is defined as the fraction of the recombinations through the τ_{sg} channel.

$1/\tau_{tt}$. The 3/4 triplet flux goes down to T_1 directly. The rate equations for exciton numbers n_S and n_{T_1} are

$$\frac{dn_{T_1}}{dt}=\frac{1}{\tau}\frac{3N}{4}+\frac{n_S}{\tau_{st1}}-\left(\frac{1}{\tau_{t1s}}+\frac{1}{\tau_{tg}}\right)n_{T_1},$$

$$\frac{dn_S}{dt}=\frac{1}{\tau}\frac{N}{4}+\frac{n_{T_1}}{\tau_{t1s}}-\left(\frac{1}{\tau_{st1}}+\frac{1}{\tau_{sg}}\right)n_S. \tag{2}$$

Also, since only one of the triplet states participates in the mixing, we can set $\tau_{st1}/\tau_{t1s}\approx 3e^{-\beta\Delta}$. In the steady state the yield $\eta_s\equiv(n_S/\tau_{sg})/(n_S/\tau_{sg}+n_{T_1}/\tau_{tg})$ is found to be

$$\eta_s=\frac{1}{4}\,\frac{4\tau_{tg}/\tau_{t1s}+1}{\tau_{tg}/\tau_{t1s}+\tau_{sg}/\tau_{st1}+1}$$
$$=\frac{1}{4}\,\frac{4(\tau_{tg}/3\tau)e^{-\beta\Delta}(\sqrt{2}A/\Delta)^2+1}{[(\tau_{tg}/3\tau)e^{-\beta\Delta}+\tau_{sg}/\tau](\sqrt{2}A/\Delta)^2+1}. \tag{3}$$

The result is independent of loose pair number N. Note that $\eta_s\rightarrow 1/4$ when the ISC rates $1/\tau_{t1s}$ and $1/\tau_{st1}$ approach zero. On the other hand, $\eta_s\rightarrow 1$ when $\tau_{tg}/\tau_{t1s}\gg 1$ while τ_{t1s}/τ_{st1} remains fixed, because all the triplet excitons decay through the singlet channel by ISC, as is the case for most inorganic semiconductors.

When the energy difference $\Delta+\Delta_2-W$ between the lowest state in the T_2 exciton band and the highest state in the T_1 band exceeds the optical phonon energy $\hbar\omega_0$, the transition between T_2 and T_1 is slowed down by the phonon bottleneck. W is the T_1 exciton bandwidth, and $\Delta_2=0.3$ eV is the energy difference between T_2 and S.[10] Now the transition from T_2 to S becomes important, and we have to generalize Eq. (2) to include the branching into S and T_1 out of T_2. When one-phonon emission is impossible, the transition can take place via either multiphonon emission due to nonadiabatic interaction or high-order perturbation. Both channels exhibit exponential dependence on the number of emitted phonons required to satisfy the energy conservation, which is proportional to the electronic energy difference. So phenomenologically we set $1/\tau_{tt}=(1/\tau)[1+e^{\alpha(\Delta+\Delta_2-\Delta_0)}]^{-1}$ and $1/\tau_{st1}=(1/\tau)(\sqrt{2}A/\Delta)^2[1+e^{\alpha(\Delta-\Delta_0)}]^{-1}$. Δ_0 is equal to $W+\hbar\omega_0$. α is taken as a tunable parameter inversely proportional to $\hbar\omega_0$. If multiphonon emission is the main relaxation mechanism, α will increase (narrower bottleneck) for smaller Huang-Rys factor S, which measures the effective triplet exciton-phonon coupling. From the emission line shapes of singlet excitons it has been shown that samples with better intrachain order have smaller S. W is estimated as follows. The bandwidths of both the conduction and valence bands are about 2 eV with similar effective masses.[10] Assuming that the effective mass theory works for the singlet exciton band, its bandwidth W_s should be about 1 eV because the exciton mass M_s is the sum of the electron and hole masses. The triplet bandwidth W is expected to be much smaller because triplet excitons are much more localized with larger effective total mass M_t. The size of the chain length dependence of the exciton energy due to quantum confinement is inversely proportional to the exciton mass. Indeed, the ratio between the T_1 and S excitons is found to be 0.3:1,[9] which implies that $W=W_s\times 0.3=0.3$ eV and $\Delta_0=0.5$ eV, with $\hbar\omega=0.2$ eV.[18] The ISC transition from $|T_2\rangle$ to $|S\rangle$ is free of such an effect, and can be approximated as simply $1/\tau_{t2s}=(\sqrt{2}A/\Delta)^2(1/\tau)$. After some algebra the yield for this three-state system becomes

$$\eta_s=\frac{1}{4}\,\frac{(4x+1)+4(\tau_{tg}/\tau_{t1s})(x+1)}{(x+1)(1+\tau_{tg}/\tau_{t1s}+\tau_{sg}/\tau_{st1})+\tau_{sg}/\tau_{st2}}, \tag{4}$$

where x denotes τ_{tt}/τ_{t2s}, and τ_{sg}/τ_{st2} can neglected because it is much smaller than 1. Equation (4) for various twist angles is shown in Fig. 2. The yield drops from 1 to 1/4 when τ_{sg} is equal to $1/\tau_{t1s}$, which is proportional to $\sin^2\theta$. So for larger θ the yield stays at 1 up to larger Δ. When θ is around the physical value of 7°, $1/\tau_{t1s}$ dominates $1/\tau_{tg}$ for

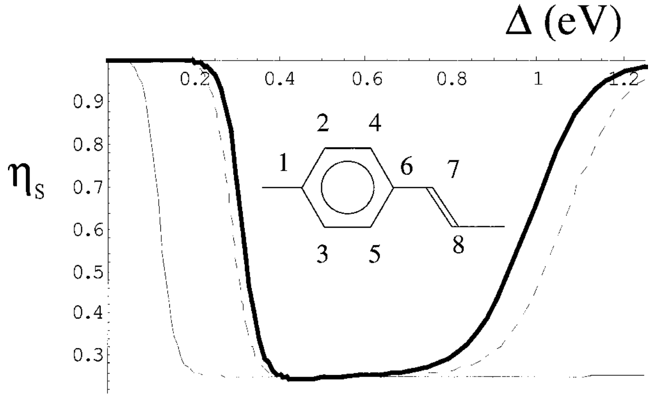

FIG. 2. The intrinsic yield η_s is shown as a function of Δ for various twist angles θ. Parameters chosen are $\alpha=15$ eV^{-1}, $\Delta_0=0.5$ eV, and $\theta=0.01°$ (thin line), 7° (dashed line), and 13° (thick line). Note the bottleneck effect at large Δ where the yield increases abruptly after a transient plateau. Inset shows the labels of carbon atoms in each repeat unit.

$\Delta < 0.3$ eV, so all excitons decay through the τ_{sg} channel and the yield is close to 1. θ can in principle be controlled by the side group, and is as large as 20° for some polymers[19]. For $0.3 < \Delta < 0.6$ eV, the yield stays around 1/4 as the recombination is spin-independent. For $\Delta > 0.7$ eV, $1/\tau_{t2s}$ dominates $1/\tau_{tt}$ due to the phonon bottleneck, so the T_2 population is forced to S and decays through τ_{sg} again. α is chosen to be 15 eV^{-1}. Other values give qualitatively similar results. The T_1 exciton energy E_{T1} was reported in a recent experiment to be around 1.6 eV.[20] Based on that the transition rate $1/\tau_{tt}$ across the bottleneck can be estimated more quantitatively by assuming that the dominant mechanism for the transition is the multiphonon emission. The multiphonon emission rate is controlled by two factors: the number of emitted phonons p_{tt} and the Huang-Rys factor S of the lattice displacement for the $T1$ exciton. The energy gap for the triplet bottleneck $\Delta_2 + \Delta - W = 1.1$ eV for $E_{T2} - E_{T1} = \Delta_2 + \Delta = 1.4$ eV (measure by induced absorption) and $W = 0.3$ eV. So $p_{tt} = 1.1/0.2 \simeq 5$ for $\hbar\omega_0 = 0.2$ eV. S is estimated by comparing τ_{tg} with τ_{st1}. Both of the processes are spin forbidden. τ_{tg} is much longer than τ_{st1} because τ_{st1} is one-phonon allowed while τ_{tg} requires p phonons. They are then expected to be related by $pS^{p-1}/(p-1)! = \tau_{st1}/\tau_{tg}$ at low temperatures.[21] Taking $\tau_{st1} = 1$ ns,[22,23] $\tau_{tg} = 70$ ms,[24] and $p = E_{T1}/0.2$ eV $\simeq 8$ for $E_{T1} = 1.6$ eV, we get $S \simeq 0.19$. We then use S to get τ_{tt} by relating it to the singlet relaxation time τ. Both of them are spin allowed and τ is one-phonon allowed while τ_{tt} requires multiphonon emission. As for τ_{st1}/τ_{tg}, the relation is $\tau_{st1}/\tau_{tt} = S^{p_{tt}-1} p_{tt}/(p_{tt}-1)!$ Using $p_{tt} = 5$, $S = 0.19$, and $\tau \simeq 1$ ps, we have $\tau_{tt} \simeq 3.7$ ns. Assuming $\tau_{t2s} \simeq \tau_{st1} \simeq 1$ ns, we find that about 79% of the T_2 excitons are redirected to the singlet sector due to phonon bottleneck, and the intrinsic yield becomes $1/4 + (3/4)0.79 = 0.84$. Our more phenomenological result in Fig. 2 also gives a similar result for $\Delta \simeq 1$ eV.[20]

There is another channel by which the singlet can mix with the triplet states, i.e., heavy atom or magnetic impurity scattering. The matrix element between the Bloch states near the band edge can be approximated by a constant independent of $k_{e,h}$. They provide an effective magnetic field which flips the spin, and adds an extra term $\hat{H}_S = g\hat{S}^+ + g^*\hat{S}^-$ to $\hat{H}_0 + \hat{H}_{so}$. Again, we can diagonalize the 4×4 matrix to find the new eigenvalues, eigenfunctions, and transition rates. The yield as a function of the effective coupling g at various Δ is shown in Fig. 3. Appreciable change occurs only when g is of the order of 10^{-2} eV. Such a scale cannot be achieved by the dipole interaction of magnetic impurities, but is within the order of spin-orbital splitting for heavy atoms.

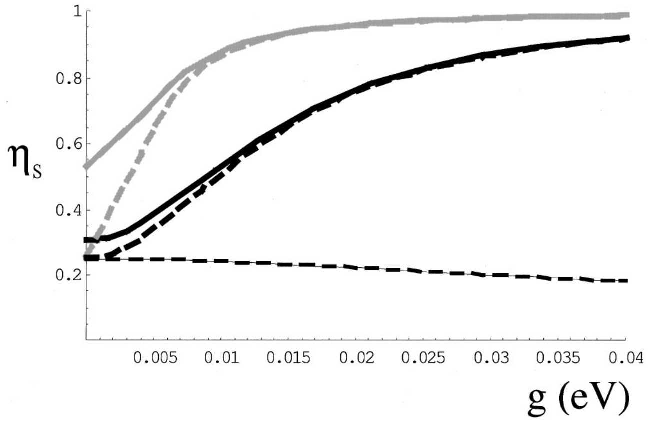

FIG. 3. The intrinsic yield η_s is shown as a function of the impurity spin-flip coupling constant g at various exchange energies and twist angles. Parameters used are $\alpha = 15$ eV^{-1}, $\Delta_0 = 0.5$ eV, and $\theta = 1°$ and $7°$ for the dashed and solid lines, respectively. For each θ, we plot three Δ values: 0.3 (gray line), 0.5 (thin line), and 0.9 eV (thick line).

In conclusion, we predict that the intrinsic EL quantum yield η_s can be close to 1 when the exchange energy is either smaller than 0.3 eV due to intersystem crossing, or higher than 0.7 eV due to phonon bottleneck. The yield can be raised when intersystem crossing is enhanced by a large ring twist angle θ (controlled by the side groups) or heavy atom impurities, or when the bottleneck is tightened by a small triplet Huang-Rys factor S (better intrachain order). These results explain the high EL measured experimentally[4] and show that the simple limit of 1/4 for the internal quantum yield does not necessarily hold.

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