# Synthesis, Excited State Dynamics, and Optical Characteristics of Oligophenyl-Based Swivel Cruciforms in Solution and Solid State

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Oligophenyl-based swivel cruciforms are an amorphous class of materials for potential use in display applications. In this work, we describe the design, synthesis, and structural and optical properties of a group of chromophores with varying degrees of  $\pi$ -conjugation that produce blue emission and high photoluminescence quantum yields (PLQYs). The swivel cruciforms are branched complexes consisting of two arms, and the relative rotation of these arms is an important factor that determines the optical properties of these systems. The studies reveal that the physical size of the system, that is, the arms, and the presence and position of functional groups results in different degrees of sterical effects. This has a dramatic impact on the interplay between nonradiative and radiative decay of the excited state. For the least  $\pi$ -extended system, control of the excited state decay can be achieved by modifying the properties of the medium through an increase in the viscosity, which is demonstrated accordingly. The data shows that an intramolecular excited state is responsible for the swivel cruciform emission in solution. The character of this "aggregate" and its emission is not dissimilar to an excimer, and we therefore attribute it to an intramolecular excimer. In the solid state, a combination of intra- and intermolecular excimers are the most likely source of the emission. The data also shows that intra molecular excimers can produce a surprisingly high PLQY, when either properties of the medium facilitate this or when functional groups introduce steric hindrance, which subsequently prevents the nonraditive decay through conformational change.

#### Introduction

Organic materials are rapidly becoming more common in various micro- and optoelectronic applications, such as organic electronics, display applications, photovoltaic devices, etc.<sup>1,2</sup> For many of these applications, the key material is an organic conjugated polymer system, especially in the case of active display applications of the light-emitting diodes (LEDs). Electroluminescence (EL) from a conjugated polymer was first realized using the poly(*p*-phenylene vinylene) (PPV) system, and this work generated an enormous momentum in the entire field of organic electronics.<sup>3–6</sup>

Although this work clearly was an unprecedented success, there still remained important problems to address and challenges to deal with. One such issue concerns the color and hue of the photoluminescence (PL) of the LED based upon organic conjugated polymers. There are a range of materials available for the yellow and red regions, but less so for the UV-blue parts of the optical spectrum. In the proceeding efforts, it was apparent that the development of stable conjugated polymer materials for the UV-blue was challenging due to the relatively large

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bandgap of the conjugated polymer in these LEDs. In addition, the color and hue of some LEDs is less well-defined due to the large extent of inhomogeneous broadening of the electronic transition, which can result in a relatively broad PL and EL spectrum. Another issue relates to the processing of these materials in the actual LED fabrication process. Conjugated polymers with a high molecular weight and high polydispersity are demanding to work with due to their low solubility. The crystallinity can be extensive in some cases. One prominent example in this context is PPV,<sup>1</sup> and hence, spin-coating of thin films in the LED fabrication procedure is more problematic. The strong tendency to form aggregates is also a serious problem with the spectroscopic properties of these, being less ideal for the LED operation because the nonradiative decay mechanisms are relatively strong upon aggregate formation.7-17 What is beneficial, though, in this context is the transport properties, which are greatly enhanced with strong intermolecular interactions, and this, in turn, is a key requirement in organic electronic devices such as LEDs.

It is therefore of great interest to be able to control the spatial packing and orientation of the active material while at the same time achieve maximum  $\pi - \pi$  overlap between separate chromophore units to maximize charge transport and device operation. This is, of course, a difficult challenge in synthetic chemistry, but some recent advances using amorphous organic materials suggest that this way forward may be rewarding. Some structures that have been considered in this context include dendrimeric forms,<sup>18–20</sup> starbust,<sup>21,22</sup> oligomers, spiro-compounds,<sup>19,20,23–25</sup> planar and swivel type cruciforms.<sup>26–32</sup>

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In this present work, we explore the photophysical and structural relationships of a series of oligophenyl-based swivel cruciforms, designed using a versatile synthetic strategy. This group of materials show unusually high PL efficiency in the UV-blue part of the spectrum, and these are attractive material properties often sought in materials for display applications. The PL properties in the steady state and time domain of solutions and films are described in this work. In complement to the spectroscopy, we have also performed theoretical calculations on a subset of the compounds. The work shows how the structure of the system can affect the optoelectronic properties and, thereby, the PL efficiency (PLQY). The work also shows the impact the properties of the medium may have on the photophysics, in some cases with dramatic effects.

#### **Materials and Methods**

**Density functional theory calculations.** The DFT calculation were performed as previously outlined.<sup>33–38</sup> Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the Becke3LYP (B3LYP)<sup>33</sup> functional. The basis set used was the 6-31G(d) Pople basis set.<sup>34</sup> All of the DFT calculations were performed with the Gaussian 03 package.<sup>38</sup>

**Optical Spectroscopy.** All compounds where dissolved in methyl cyclohexane (MCH) unless otherwise stated. Thin films were obtained on quartz disks by spin-coating solutions of ~15 mg/mL solvent spun at 1500 rpm for 30 s. Absorption spectra were measured on a Perkin-Elmer Lambda 19 spectrophotometer, and the steady state PL was recorded using a Jobin Yvon Horiba Fluoromax 2. The PLQYs in solution were calculated using the comparative method<sup>39</sup> with anthracene/ethanol as the standard, both sample and standard with absorbencies ~0.1 OD.

For thin films, the PLQYs were measured as outlined by de Mellow et al. and Pålsson et al.<sup>40</sup> In the low-temperature measurements, a liquid nitrogen cryostat (JANIS) was used. The time-resolved PL was measured using the time-correlated, single-photon counting technique (TCSPC) described recently,<sup>41</sup> except that here, the excitation source consisted of a modelocked cavity dumped (APE Pulse switch) Ti:Saphire laser (MIRA, Coherent). Near-infrared optical pulses with a temporal width of  $\sim 100$  fs (fwhm) were used to generate the third harmonic generation UV pulses at a wavelength of  $\sim 300$  nm with an Inrad (model 5-050) harmonic generator. The PL was detected using a single-photon counting module based upon an avalanche photo diode (Id Quantique model 100-50) linked to a time-to-amplitude converter (Ortec 567) and multichannel analyzer (E.G. & G. Trump Card and Maestro for Windows v. 5.10). The instrument response function (IRF) of the apparatus was measured from the Rayleigh scattered light, giving an IRF with a duration of  $\sim$ 125 ps fwhm. All PL decays were recorded to a minimum of 10 000 counts in the peak channel of the pulse height analyzer. The data was analyzed using the standard method of iterative reconvolution and nonlinear least-squares fitting in a Microsoft Excel spreadsheet.<sup>41</sup> The quality of the calculated fits was judged using statistical parameters, including the Durbin-Watson parameter, reduced  $\chi^2$ , random residuals, and autocorrelated residuals. The experimental data were subsequently fitted to a sum of exponentials,

$$F(\lambda_{\rm em}, t) = \sum_{i} A_{i}(\lambda_{\rm em}) \cdot e^{-k_{i} \cdot t}$$
(1)

## Results

Synthesis and Structural Characterization. Synthesis of swivel-type cruciforms has been an active topic during recent

SCHEME 2: Synthesis of the Extended Swivel Cruciforms SC5 and SC7.



years.<sup>26–32</sup> These oligomers are based on tetrasubstituted biaryl cores, such as binaphthyl-,<sup>31</sup> biphenyl-,<sup>42–45</sup> or bithienyl<sup>46,47</sup> cores.

Compared to Bunz's<sup>26–29</sup> and Nuckolls's<sup>30</sup> planar cruciforms, these swivel type cruciforms allow, at least in principle, rotation between the biparyl moieties and within the homologous parts of the molecule, which we call the "arms" of the cruciforms. This should, in principle, lead to a greater degree of conformational freedom. However, in the swivel cruciform architectures designed by Farrell and Scherf, it was found that the three-dimensional arrangement of these structures could be biased by introducing the possibility for  $\pi - \pi$  interactions to occur.<sup>42</sup> For example, it was found that the cruciform **SC3a** shown in Scheme 1 adopts a folded configuration in the crystal structure and that this type of foldamer is also retained in solution.

All syntheses of swivel cruciform dimers follow a similar straightforward method utilizing the different reactivity of aromatic bromo/iodo and chloro groups in a Suzuki-type, aryl—aryl, cross-coupling reaction (Scheme 1).<sup>48–50</sup> The synthetic strategy toward the sterically hindered terphenyl based cruciform **SC3b** follows the strategy developed by Farrell and Scherf with the isolation of the chloroaryl precursor 3 (Scheme 1) from the reaction of 1-chloro-2,5-dibromobenzene with 3,5-bis-*tert*-butyl-phenylboronic acid under microwave or conventional conditions, or both.<sup>51,52</sup>

Within the initial step, a chloroaryl precursor (here **3**; see Scheme 1) is formed by reacting 1-chloro-2,5-dibromobenzene with 3,5-bis-*tert*-butyl-phenylboronic acid under microwave or conventional conditions<sup>51,52</sup> in good yields, which is subsequently homocoupled in a nickel-mediated Yamamoto-type reaction<sup>53</sup> toward the desired cruciform. The syntheses of **SC3a** and the corresponding monomeric terphenyl derivative (**SC1**) have been reported in an earlier paper and are also depicted in Scheme 2 for better understanding.<sup>42,49</sup> Although **SC1** is, strictly speaking, not a cruciform, we will use this notation throughout the text for reasons of consistency.

Despite its twisted structure, **SC3a** shows a tendency to crystallize. Optimization of the thermal properties would seem to be necessary with respect to potential use in optoelectronic applications such as LEDs. The easiest way to obtain an increased amorphous character is to enlarge the sterical hindrance of the arms so that internal folding and crystallization are prevented. **SC3b** as an analogue to **SC3a** exhibits an increased steric hindrance due to additional *tert*-butyl groups on the outer phenyl rings.

Synthesis of extended swivel cruciforms requires additional steps. To increase the arm length, we have prepared a versatile central building block 7 that can be reacted with a broad variety of substituents and is still of current synthetic interest. To prepare building block 7, 1,4-dibromo-2-chlorobenzene (2) was coupled via a Suzuki type cross coupling reaction with 4-trimethylsilyl-phenylene-boronic acid (5) giving 1-chloro-2,5-(trimethylsilyl-phenyl)benzene (6) in more than 75% yield after recrystallization from heptane/dichloromethane. No further purification is needed at that step.

The TMS protected terphenyl **6** was subsequently converted to the diiodo derivative **7** by treating **6** with ICl in yields close to 90%. Subsequent Suzuki type cross-coupling with the corresponding boronic acid/ester allows access to a broad variety of swivel cruciform arms. Within this publication, 3,5-bis-*tert*-butylphenyl-pinacolatoboronate (**1**) and 2-(9,9-di-*n*-dioctylfluorene)-4,4',5,5'-tetramethyl-1,3,2,dioxaborolane (**8**) have been coupled to building block **7**, leading to the cruciform precursors **9** and **10**. The synthetic protocol for the preparation of the corresponding cruciforms **SC5** and **SC7** is similar to that used in the preparation of **SC3a** and **SC3b** by utilizing a nickel-mediated, Yamamoto-type, aryl-aryl coupling reaction under microwave conditions.<sup>53</sup>

All swivel cruciform materials were obtained in reasonable yields and were purified via column chromatography. Structural integrity was proved via NMR spectroscopy and MS, respectively.



Figure 1. Solution <sup>1</sup>H NMR spectra in the aromatic region of SC3a (bottom) and SC3b (top) in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.

All swivel type cruciforms and intermediate products show good solubility in common solvents, which allowed a detailed characterization of all materials by NMR spectroscopy. This method also allows judging of the strength of interaction between the cruciform arms. As mentioned previously,<sup>42</sup> **SC3a** shows a strong  $\pi - \pi$  stacking of two phenyl-rings, which is proved by the high-field position of two directly coupled doublets at  $\delta = 6.51$  and 6.93 ppm with a coupling constant of 8.5 Hz. As expected, the upfield shift of the signals cannot be found in the related **SC3b**, as shown in Figure 1, displaying that there is no significant  $\pi - \pi$  interaction of the arms in solution.

The crystal structure of **SC3b** was obtained from solutions in dichlormethane or THF, respectively, and investigated by X-ray diffraction at room temperature. Analysis of **SC3b** shows that there is no folded helical conformation, as in **SC3b** in the solid state. The large distances between the outer phenyl rings can be clearly seen in n the top view of **SC3b** shown in Figure 2.

**Density Functional Theory Calculations.** To learn more about the structure and function relationship, density functional theory (DFT) calculations were performed on **SC3a** and the related system **SC3b**. These procedures resulted in energy-minimized conformations of the two systems, and the calculations reveal that there is a nonzero dihedral angle between the phenyl rings structures within the two terphenyl arms in both **SC3a** and **SC3b**. The relative distortion of the two terphenyl arms in **SC3a** is at an angle of  $\sim 30^{\circ}$ . Equally, for **SC3b**, the arms containing the phenyl rings are crossed, but the relative distortion angle in this case is  $\sim 40^{\circ}$ . Figures 3 and 4 show the optimized configurations for the **SC3a** and **SC3b**, respectively. Also shown in both figures are the frontier electronic orbitals for the HOMO and LUMO states. These show, for both systems, that although the HOMO appears to be confined to one arm

exclusively, the LUMO is delocalized over both arms in the cruciform structure. In parallel, we also calculated the gas phase HOMO–LUMO energy gap for both systems. For **SC3a**, the energy gap was 5.39 eV ( $43478 \text{ cm}^{-1}$ ), and for **SC3b**, the energy gap was 4.55 eV ( $36630 \text{ cm}^{-1}$ ).

We note that the optimized structures as obtained in the DFT calculations are close to conformations of **SC3b** as seen in the crystal structure (Figures 2 and 4). Regarding the HOMO–LUMO energy gap, the experimentally measured  $S_0 \rightarrow S_1$  transitions show a slight difference for **SC3b** and larger difference for **SC3a**. We attribute this difference to the calculations' essentially being performed in a vacuum, whereas the optical measurements (excitations) have been performed in a dielectric medium with distinctively different properties.

**Optical Spectroscopy.** Figure 5 shows the absorption and PL of the different swivel cruciform molecules in solution and solid state (films) at ambient temperatures. The data shows that there is a steady progression of the absorption maximum toward longer wavelengths with an increasing size of the  $\pi$ -electron system. For **SC3a**, the long wavelength absorption maximum is located at ~275 nm (35714 cm<sup>-1</sup>), but for **SC5**, it is located at ~295 nm (33898 cm<sup>-1</sup>), and for **SC7**, the position is ~330 nm (30303 cm<sup>-1</sup>). The PL, on the other hand, is concentrated to a spectrally narrower region and centered in the 380–390 nm range for all swivel cruciforms **SC3a**, **SC5**, and **SC7**.

The Stokes shift of the swivel cruciforms also varies accordingly with the extent of the  $\pi$ -electron system, as can be concluded from the data in Table 1, with **SC3a** showing the largest Stokes shift, followed by smaller shifts for **SC5** and **SC7**. In addition, the PLQY depends strongly on the size of the  $\pi$ -electron system as well as the temperature. Table 1 displays the data of PLQYs for the various swivel cruciforms at ambient temperatures, and Figure 6 shows the PLQY,  $\phi_f(T)$ , as function of temperature in the temperature range 300–80 K. The data



Figure 2. Two perspective views of the molecular structure of compound SC3b.

show the presence of a temperature-dependent nonradiative decay channel, in particular for the form **SC3a**.

To better understand the photophysics of the swivel type cruciforms SC3a, SC5, and SC7, the related compounds SC3b and SC1 where tested in a similar fashion. In Figures 7a and 8a, the absorption and PL of the solutions are shown. The absorption spectrum of SC3b shows, apart from the main band, a long wavelength absorption band indicative of more than one absorbing species. However the PL of SC3b is, on the other hand, broad and devoid of structure, as in the case of SC3a. For the compound SC1, on the other hand, we observe a broad, nonstructured absorption, and the PL spectrum exhibits a wellresolved vibronic progression with peaks at 332, 347.5, and 362 nm. This corresponds to an energy separation of 1343.5  $cm^{-1}$ between the higher and the middle peak; the energy separation between the middle peak and the lowest is 1153 cm<sup>-1</sup>. SC1 was also investigated in a more polar environment. A measure of solvent polarity can be given by the solvent density parameter,  $\Delta f$ ,

$$\Delta f = \left(\frac{\varepsilon_{\rm r} - 1}{2\varepsilon_{\rm r} + 1} - \frac{n_{\rm D}^2 - 1}{2n_{\rm D}^2 + 1}\right) \tag{2}$$

, where  $\varepsilon_r$  is the dielectric constant and  $n_D$  is the refractive index. For MCH,  $\Delta f \approx 0$ , whereas for ethanol,  $\Delta f = 0.29$ , which is a relatively high value, indicating a fairly polar dielectric medium. Figure 8a shows that changing the dielectric constant of the medium has little impact on the absorption maxima or the fine structure of the PL spectrum. The PLQY of these two compounds was found to be remarkably high, as Table 1 shows, with values of 0.82 and ~1.0 for **SC3b** and **SC1**, respectively. Accordingly, there was also a moderate to insignificant temperature dependence on the PLQY of these two materials (data not shown). Interestingly, we also found that the PLQY of the form **SC1** is completely media-independent. Measurements in both polar and nonpolar media, as described previously, returned the same value (see table 1).

Figure 5b shows the absorption and PL of the swivel cruciforms in the solid state (films). As expected for low crystallinity materials, there is moderate impact on the absorp-



**Figure 3.** Frontier molecular orbitals calculated for **SC3a** showing the HOMO configuration (below) and corresponding LUMO configuration (above). See text for details.

tion when going from solution to solid state. The absorption maximum and the shape of the absorption band remain essentially unchanged for SC3a. However, for SC5 and SC7, there is a bathochrome shift of  $\sim 1000 \text{ cm}^{-1}$ , which is the only observed difference. The PL spectra are also affected by the change of state and, in particular, the PL of SC5 and SC7. The PL maxima of both these swivel cruciforms are red-shifted relative to the corresponding solution spectra (table 1). A significant broadening of the PL for all three systems, SC3a, SC5 and SC7, is observed for the films as compared with the corresponding solution spectra. In addition, the PLQY is affected by the change of state; we observe a reduction for all swivel cruciforms. The related compound SC1 shows a similar behavior when going from the solution to the solid state, with only a small impact on the absorption, whereas the PL is bathochrome shifted. For SC3b, there is no impact on the position of the absorption and PL maxima, although an extra red-shifted feature appears in the film, thus reflecting the fully amorphous character of the films made from this highly substituted swivel cruciform (see the Discussion and Table 1 for details).

The time-domain measurements of the PL decay provide more information about the excited state decay mechanisms. Table 2 lists the data obtained from an analysis of the PL decay of all swivel cruciforms in solution and the solid state for selected detection wavelengths. The PL decays and the nonexponential fits are also shown in Figures 7–10. The data are fitted to a sum of exponentials according to eq 1, and we found that in general, two or three exponential terms are needed to get an acceptable fit of the data. In some cases, a fast component of ~60 ps was observed. We remark that due to the time resolution of our detection system, this decay phase (when observed) is very likely not well-defined by the analysis. Hence, we also recognize that even faster decay phases in the PL dynamics could be present but that these accordingly may have escaped detection.





**Figure 4.** Frontier molecular orbitals calculated for **SC3b** showing the HOMO configuration (below) and corresponding LUMO configuration (above). See text for details.

Not included in Table 2 is the temperature dependence of the time-resolved PL. The impact of the temperature is particularly dramatic for **SC3a** in solution, as can be seen in Figure 9a. Already at 200 K, the long-lived decay component for this system has increased to 5.7 ns, whereas for **SC5** and **SC7** in solution, there is hardly any impact at all. For **SC3b**, the PL lifetime increases from 1.3 to 4.0 ns as the temperature is lowered from 300 to 100 K. For **SC1**, on the other hand, there is no impact of the temperature on the PL dynamics.

## Discussion

When comparing the optical data of SC3a, SC5, and SC7, one can derive a correlation between size and extent of the  $\pi$ -electron systems, the degree of substitution, and the optical characteristics. This correlation is clearly observed in the apparent Stokes shift of the emission and the number of phenyl rings in the cruciform structures. We observe that SC3a has the largest Stoke shift; SC7 shows the smallest, and SC5 is intermediate. The implication is that the least extended system, SC3a, has a large degree of structural relaxation in the excited state, which successively is reduced as the extent or the size of the  $\pi$ -electron system is increased and, thus, introduces sterical



Figure 5. Absorption and luminescence of the swivel cruciforms in solution and film. See text for details.

 TABLE 1: Data of the Optical Transitions and PLQYs in Solution and Solid State<sup>a</sup>

compound	$\tilde{\nu}_{abs} \ (cm^{-1})$	$\tilde{\nu}_{\rm em}~({\rm cm}^{-1})$	$\Delta \tilde{\nu} \ (\mathrm{cm}^{-1})$	φ <sub>f</sub> (300 K)
SC3a/MCH	35 714 (280)	25 316 (395)	10 398	0.10
SC5/MCH	33 898 (295)	25 975 (385)	7 923	0.75
SC7/MCH	30 303 (330)	25 316 (395)	4 987	0.82
SC3a film	35 714 (280)	25 316 (395)	10 398	0.04
SC5 film	32 787 (305)	25 006 (400)	7 781	0.15
SC7 film	29 154 (343)	23 529 (425)	5 625	0.30
SC3b/MCH	35 714 (280)	26 667 (375)	9 047	0.82
SC3b film	35 714 (280)	25 974 (385)	9 740	0.18
SC1/MCH	35 336 (283)	30 030 (333)	5 306	0.98
SC1/EtOH	35 336 (283)	30 330 (333)	5 306	1.00
SC1 film	36 101 (277)	28 169 (355)	7 932	0.40

<sup>*a*</sup> Numbers in parentheses are the corresponding wavelength in nm. The Stokes shift is calculated from  $\Delta \tilde{\nu} = \tilde{\nu}_{abs} - \tilde{\nu}_{em}$ . MCH is methylcyclohexane, and EtOH is ethanol. See text for further details.



**Figure 6.** Temperature dependence of the three cruciforms in solution. The symbols represent the measured data, and the line is a fit of data using eq 3. See text for details.

hindrances in the relaxation process. In the same context, we note that the related systems **SC3a** and **SC3b** have nearly the same Stokes shift and that the absorption and PL maxima for these systems are very similar. The implication is therefore that the main contribution to the Stokes shift originates from the

size of the  $\pi$ -conjugated system (number of phenyl units in each branch of the molecule). It is interesting to note that the absorption maximum of **SC3a** is very similar to the monomeric form **SC1**. The PL of **SC3a** is, however, bathochrome-shifted, and the spectrum is broad and devoid of any fine structure, which was observed for **SC1**. This suggests that the PL of **SC1** is essentially due to  $S_1 \rightarrow S_0$  fluorescence.

Semiempirical calculations reveal that the ground state dipole moment for SC1 is small,  $\mu_{dip} < 1$  D. As a consequence, intramolecular dipole-dipole ground state interactions between the two arms in SC3a must therefore also be weak, which would explain why the absorption maximum of SC1 and SC3a is nearly the same. However, there are clearly interactions in the excited state, and the data suggest that an intramolecular excited state aggregate is formed. Support for this conclusion comes from the broad and red-shifted PL spectrum (relative to SC1) as observed for SC3a and from the DFT calculations in which the LUMO was found to encompass both arms in SC3a. The features of the emission of this excited state aggregate are similar to what is commonly observed for a classical excimer or exciplex, the redshift and the absence of vibronic structure. Because there is no evidence for any ground state interactions, we therefore suggest attributing this emission to an intra molecular excimer. In solution, we rule out any intermolecular excimer formation because the solution is too dilute for this to occur ( $\sim 10^{-6}$  M). The data from the time-resolved PL experiments also support this idea. We observed that the PL dynamics is more than two times slower in SC3a, as compared with SC1, which is consitent with the formation of intramolecular excimers and the associated PL emission process.

More information about the excited state properties can be obtained from the temperature dependence of the PL, as shown in Figure 6. There is a dramatic increase in the PLQY at lower temperatures for **SC3a**, whereas the other two systems, **SC5** and **SC7**, show less temperature dependence. This strong temperature dependence suggests that the excited state undergoes structural changes in which the relative orientation of the branches is affected, subsequently leading to a nonradiative decay of the excited state. The temperature dependence suggests that there is an associated activation energy,  $E_a$ , for this nonradiative decay mechanism. This activation energy is related to the PLQY  $\phi_f(T)$  according to the relation<sup>54</sup>



Figure 7. Absorption and luminescence of the cruciform SC3b in solution and film. See text for details.



Figure 8. Absorption and luminescence of the cruciform SC1 in solution and film. See text for details.

$$\phi_{\rm f}(T) = (A + B \cdot e^{-E_{\rm a}/k_{\rm B}T})^{-1}$$
(3)

, where A and B are arbitrary constants. The fit of the data (see Figure 6) and subsequent analysis gives an activation energy for SC3a of 5.6 kJ/mol; for SC5 and SC7, the activation energy is 9.7 and 10.1 kJ/mol, respectively. For SC3a, this means that the activation energy,  $E_a = 58$  meV, is close to the thermal energy;  $k_{\rm B}T = 26$  meV at T = 300 K, and conformational changes can therefore be thermally activated. Interestingly, the related structures SC3a and SC3b showed very different temperature dependence. At ambient temperatures, SC3b has, in contrast to SC3a, a relatively high PLQY that rises slightly at lower temperatures, but its temperature dependence is more moderate and more complicated as compared with SC3a (data not shown). For this reason  $E_a$  could be determined for SC3b only. This behavior indicates more sterical hindrance for SC3b as compared with SC3a but similar dependence as for SC5 and SC7.

Direct measurements of the excited state kinetics provided more information about the interplay between radiative and nonradiative decay channels. In the PL decay, a fast component is observed in solution, and this decay time is on the order of 60-70 ps. This phase is observed for SC3a, SC5, and SC7.

TABLE 2: Data of the Time-Resolved PL for the Swivel Cruciforms in Solution and Film, and for Excitation at 290  $nm^a$ 

Compound	$\lambda_{\rm em}$ (nm)	$\tau_1$ (ns)	$A_1$	$\tau_2$ (ns)	$A_2$	$\tau_3$ (ns)	$A_3$
SC3a/MCH	340	0.07	0.150	1.60	0.090		
	420	0.07	0.060	1.79	0.050		
SC3a film	340	0.11	0.042	0.87	0.016	3.30	0.034
	440	0.31	0.031	1.53	0.030	3.70	0.026
SC5//MCH	340	0.10	0.060	1.70	0.027		
	440	0.07	0.040	1.81	0.032		
SC5 film	340	0.06	0.092	0.36	0.026	1.12	0.016
	420	0.33	0.024	1.00	0.008	4.40	0.015
SC7//MCH	360	0.06	0.100	0.66	0.050		
	440	0.07	0.019	0.71	0.056		
SC7 film	380	0.06	0.140	0.41	0.061	0.71	0.041
	420	0.16	0.041	0.46	0.095	0.93	0.022
SC3b/MCH	390	1.35	0.023				
SC3b film	350	0.26	0.039	1.30	0.045	3.80	0.029
	450	4.31	0.070				
SC1/MCH	360	0.07	0.120	0.75	0.140		
SC1 film	340	0.42	0.080	1.14	0.027		
	400	1.21	0.110	4.79	0.010		

<sup>*a*</sup> The data are fitted to a sum of exponentials according to eq 1. All the data are recorded at ambient temperatures, 300 K. See text for details.



Figure 9. Time-resolved PL of the swivel cruciforms in solution and film. For the solutions, the PL decay is also recorded at different temperatures. The PL is recorded in the maximum of all the systems and for all the conditions. See the text for details.



Figure 10. Time -resolved luminescence of the SC3B and SC1 in solution and film. For the solutions, the luminescence decay is also recorded at different temperatures. The luminescence is recorded in the PL maximum of all the systems and for all the conditions. See the text for details.

As the data in Table 2 show, there is little detection wavelength dependence in this phase, and we therefore attribute it to planarization of the phenyl rings within the arms of the swivel cruciforms.<sup>32</sup> We note that this decay phase is also observed for the form SC1, but for the more sterically hindered system **SC3b**, such a fast decay of the PL is not present. Although the two more extended cruciforms SC5 and SC7 had a largely temperature-independent PL decay, SC3a undergoes dramatic changes, in particular when the more long-lived decay phase of the PL is monitored. The PL decay dynamics of SC3a changes by a factor of 3.6 as the temperature is lowered from ambient to cryogenic temperature regions (100 K), and the decay is completely dominated by the long-lived component. For SC3b, the same scenario is observed, but with a slightly less dramatic change in the longest lifetime by a factor of  $\sim 2$ . For SC1, there is, on the other hand, no temperature dependence on the excited state decay. In view of the high PLQY for this system, this is an expected result. The PLQY,  $\phi_{\rm f}$ , and the PL decay are related and connected properties through the relation

$$\phi_{\rm f} = \frac{k_{\rm F}}{k_{\rm F} + \sum k_{\rm nr}} \tag{4}$$

, where  $k_{\rm F}$  is the rate of the radiative PL decay and  $\Sigma k_{\rm nr}$  denotes the nonradiative decay routes. Because we in this case can assume that the nonradiative decay is temperature-dependent (i.e.  $\Sigma k_{nr} = k_{nr}(T)$ ), we can rationalize the increase in the PLQY,  $\phi_{\rm f}$ , at lower temperatures with a strong decrease in the nonradiative decay rate  $k_{nr}(T)$ , even though  $k_{\rm F}$  also decreases. In passing, we note that intersystem crossing  $(k_{isc})$  to a triplet state can also affect the  $\Sigma k_{nr}$  decay routes. However, we have observed that the amount of phosphorescence is insignificant when compared to the fluorescence or excimer PL, and it is hence safe to assume that  $k_{\rm isc} \approx 0$ . Therefore, it is fair to conclude that the PL is completely dominated by fluorescence or excimer PL, at least under the experimental conditions used in this study.<sup>32</sup> Because the PLQY of SC1 was larger than that of SC3b, this suggests that there is still some degree of nonraditive decay of the excited state in SC3b, which must then be due to conformational relaxation of the branches in the excited state of **SC3b**. It is therefore also interesting to note that the *tert*-butyl groups attached to the phenyl units of SC3b have a dramatic impact on the extent of excited state conformational relaxation, clearly in contrast to the case of SC3a.

The DFT calculations provide further insight into the relationship between structure and function regarding the excited state dynamics of **SC3a** and **SC3b**, as previously discussed. For both these systems, the LUMO appears to be delocalized over both arms, and this is significant when we consider the results of the optical spectroscopy. The difference in structure between these two systems is one extra *tert*-butyl groups on each terminal phenyl rings on **SC3b**, and this has the effect of introducing steric hindrance. There is accordingly limited room for relative rotations between and within the arms in **SC3b**, which is also evident when one considers the optimized conformation as seen in Figure 4.

In contrast, **SC3a** has a less compact structure, and hence, there is more room for relative motions of the two arms to occur. This was evident when the calculations where performed because it was considerably more demanding to find the optimized structure of **SC3a**. On the basis of the DFT calculations, we can therefore conclude that at ambient temperatures, the two arms in **SC3a** can rotate more freely relative to each other, as compared with the related systems **SC3b**. This is also

reflected in the absorption spectra because **SC3a** has a broader band devoid of any fine structure, which is indicative of a larger number of subconformations with their inherent variations of the  $S_0 \rightarrow S_1$  transition. Because the LUMO is delocalized over both arms in **SC3a** in its the frozen configuration, the rotations will therefore have a dramatic impact on the excited state, with strong nonradiative decay, which is implied by the low PLQY at 300 K. Lowering the temperature will then have the effect of increasing the viscosity of the medium, which will hinder rotations, thereby locking the conformation of **SC3a** closer to its optimized geometry. As a consequence, the PLQY increases in parallel to an increased PL lifetime, as can be seen in Figures 3 and 6, which was concluded earlier.

In this context, it should be mentioned that no DFT calculations were performed on the two more extended analogues SC5 and SC7. The motivation for this is the less pronounced temperature dependence in these two systems that indicates to us that there is significantly less relative rotation of the two arms, primarily due to the increased friction in the condensed phase. Hence, there is less nonradiative decay caused by conformational change in those two systems already at ambient temperatures. In this context, it is relevant to consider the hydrodynamic impact rotations in viscous medium may have on these processes. The relative rotation of the arms as in these systems is, as far as we know, experimentally difficult to assess because the impact of steric hindrance cannot be correctly quantified. However, the rotational diffusion can give us some guidience of the impact due to the physical size of these systems, assuming spherical shapes. Using the Stokes-Einstein-Debye relation,

$$D_{\rm s} = \frac{k_{\rm B}T}{6\eta V} \tag{5}$$

the size-dependent rotaional diffusion coefficient can be calculated. For the arm that is **SC3a**, we find that the rotational correlation time will be on the order of 3–4 ns, which is close to the PL lifetime. For the more extended systems **SC5** and **SC7**, on the other hand, the rotational diffusion time will be on the order of tens of nanoseconds, which is well beyond the PL lifetime in solution of these two systems. On this basis, we can therefore rationalize the difference in nonradiative decay through arm rotations for **SC3a**, as compared with **SC5** and **SC7**.

Interestingly, we observe that going from solution to solid state (films) did not result in any significant changes in the Stokes shift of the structures SC3a or SC5. The form SC7, though, did show a slightly larger Stokes shift, caused mainly by a bathochrome shift of the PL maximum relative to the corresponding solution spectrum. Similar observations were made in studies on related oligothiophene cruciforms based on that performed by Pina et al.55 In that study, solid state films where fabricated from oligothiophene chromophores dispersed in a Zeonex matrix, and although intermolecular interactions (dipolar) were considered probable, no shift of the absorption maxima was observed.<sup>55</sup> However, bathochrome shifts were observed in drop-cast films of these oligothiophene cruciforms.55 These are significant observations in view of the results obtained here, particulary because in this work, the systems where not dispersed in a matrix before the films were fabricated. Instead, the films were prepared by allowing the solvent to evaporate, which likely would result in even closer packing of chromophores.

Accordingly, the data obtained from the films, in particular the absorption data, suggest that there is no formation of ground state aggregates, such as physical dimers or higher aggregates. These aggregates would reveal themselves through a significant bathochrome shift of the absorption maxima or, more likely, a new band (Davidov splitting). The slight bathochrome shift that was observed for SC5 and SC7 could instead be due an environmental effect. The same data therefore also imply that intermolecular dipole-dipole interactions in the films are weak and insufficient to form physical aggregates. The fact that the permanent dipole moment of **SC1** is small ( $\mu_{dip} < 1$  D), which in turn implies small permanent dipole moments in SC3a and its extended analogues SC5 and SC7, supports this assumption. There is accordingly not the prerequisite in the shape of a large permanent dipole moment for the formation of physical aggregates in these systems, either. For **SC3a**, there are, however, clearer indications for the formation of an intermolecular excited state aggregate in the films. The absence of any new low-energy bands, spectral shifts, or broadening in the absorption and the observed dramatic broadening of the PL (relative to the solution spectra of SC3a) points to the formation of excited state species such as excimers. This is also in agreement with the conclusions made in ref 55. On reflection, the observations made on SC1 and SC3a in solution, and for SC3a films, show a progression from fluorescence of the monomer (SC1) to the intramolecular excimer emission from SC3a in solution. Finally, in the solid state, there is a mixture of inter- and intramolecular excimers being responsible for the PL of SC3a films.

The excited state decay of the films monitored through the time-resolved PL is more complicated than the corresponding solution measurements. This difference is due to the packing of chromophores in the films, which stimulates additional excited state decay mechanisms. The solid state therefore makes it unlikely that the decays reflect conformational relaxation because the free volume is not available to facilitate this. In addition, we also refer to the very high solution PLQYs, particularly for SC5 and SC7, which indicates a rigid structure, and this should also prevail for these two systems in the solid state. Also for SC3a, we rule out conformational relaxation as contributing factor to the reduction of that already low PLQY in going from solution to films. Because this system will also be tightly packed in the solid state, the free volume to facilitate rotation of the arms is not available. Therefore, the reduction of the PLQY in films as compared with the low temperature solution phase is due to a different effect, as will be discussed in the following paragraph.

The complex behavior of the excited state decay for SC3a, SC5, and SC7 is very likely due to electronic energy transfer (EET) through a weak Förster coupling mechanism between adjacent chromophores. In the solid state, the amorphous character of these materials will result in an inhomogeneous distribution function of the energy in the  $S_0 \rightarrow S_1$  transition, and within this inhomogeneous distribution function, there will be EET from blue to red, which will explain the wavelengthdependent PL dynamics. Inspection of the data in Table 2 shows that also in the solid state, a fast decay of 60-160 ps can be detected; however, this is for blue detection wavelengths only. For red detection, the fast component is clearly longer when the individual system is considered. This is in contrast to the solution case, and we therefore attribute this fast component observed in films as due to EET. The intermediate component observed in the films is very hard to assign because it varies rather unsystematically with system and sometimes with detection wavelength. In addition, it has a very random intensity variation which further complicates the interpretation. However, a plausible source of this intermediate decay phase could be intramolecular excimer emission, as was observed in the solution meaurements.

The presence of EET within the inhomogenous distribution function will also explain the reduction in the PLQY observed when going from solution to the solid state (films). Solid state quenching is observed in a number of cases and not clearly understood. However, we lean toward an explanation of the EET to trapped or defect states that will quench the PL as an explanation for the reduction of the PLQYs in the solid state, relative to the solution cases. The tighter chromophore packing of the film will promote EET, and the likelihood of the migrating exciton reaching such a state is therefore high in the solid state. However, for the emissive systems, the very likely source of the emission is excited state aggregates such as excimers, mainly of intermoloecular nature but possibly with some contributions from intramolecular excimers, as previously stated. This is supported by the fact that the PL film spectra are very broad and structureless and that the PL decay is relatively long-lived.

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**Supporting Information Available:** A detailed description of the synthetic protocol of all swivel cruciforms. This material is available free of charge via the Internet at http://pubs.acs.org.

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