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Siloxanes with Pendent Naphthalene Diimides: Synthesis and Fluorescence Quenching

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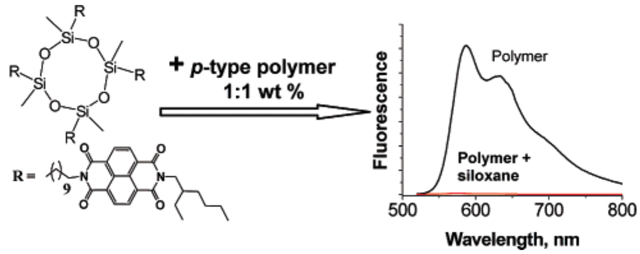
ABSTRACT



Cyclic siloxanes with pendent naphthalene diimide groups were synthesized via hydrosilylation to form amorphous electron-accepting compounds. Photophysical measurements and >99.9% fluorescence quenching of well-known *p*-type polymers by the siloxanes demonstrate that these siloxanes form a new class of highly efficient *n*-type materials that provide some control over intermolecular interactions.

Over the past decade, there has been a rapidly increasing interest in the development of organic optoelectronic materials. In the devices based on these materials the overall order, any structural defect, $\pi-\pi$ stacking, and (partial) crystallization of the material pose constraints on the usefulness of such a material.[1] While *nanoscopic* phase separation is essential for the proper performance of, e.g., organic photovoltaic solar cells, *large-scale* crystallization and stacking are not desired. In this case, both phase separation between *n*- and *p*-type materials and $\pi-\pi$ overlap domains with length scales on the order of the exciton diffusion length are desired for an effective charge separation.[2] There have been many attempts to bring controlled order to organic optoelectronic materials, and thus improve the morphology of the active materials used for organic FETs,[3] LEDs,[4] and photovoltaic devices.[5] Our interest is focused on the prevention of *large-scale* crystallization and $\pi-\pi$ stacking, and we aim to obtain a homogeneous morphology of the photoactive layer by developing amorphous materials. Recently, we reported[6] the synthesis and optoelectronic properties of a novel *n*-type amorphous tetrahedral tetraphenylmethane-based molecule, which yielded upon mixing with *p*-type

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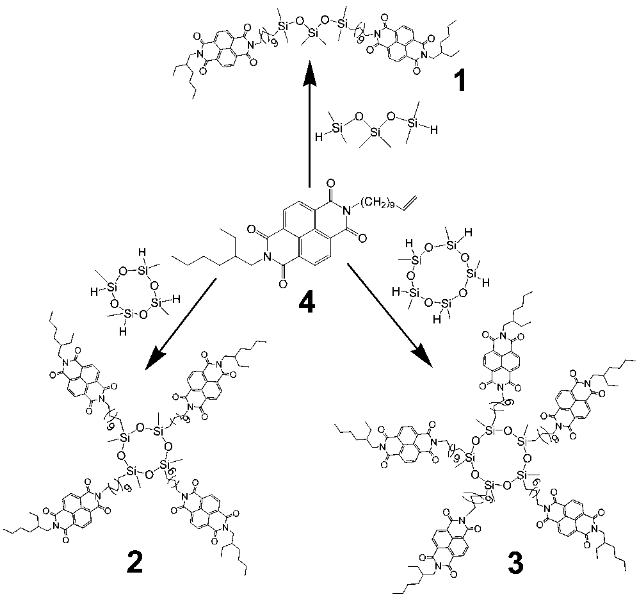
polymers a homogeneous morphology and a very high conductivity in time-resolved microwave conductivity experiments. While the resulting blend was amorphous in nature, the structural rigidity of this molecule precluded further optimization of the charge-transfer paths. Therefore we aimed to develop amorphous *n*-type materials in which the electron-accepting moieties are attached to an inert core via a flexible linker. This should allow intra- and intermolecular structural reorganization that may lead to better $\pi-\pi$ overlap between adjacent molecules, and thus to more efficient charge-transfer channels, without compromising the amorphous nature of the material. Siloxanes are attractive for this purpose, as they have a flexible, yet photochemically and electrically inert backbone. Cyclic oligomeric siloxanes provide the additional benefit of a well-defined size-dependent structure. While they have been used for ion transport,[7] liquid crystalline materials,[8] and organometallic reactions,[9] this class of materials has, as of yet, not been used in optoelectronic materials. As part of our strategy we therefore report on the synthesis, characterization, and photophysical properties of three novel siloxanes with pendent naphthalene diimide (NDI) chromophores (**1**−**3**; Scheme 1), together with their fluorescence quenching of *p*-type polymers.

Scheme 1. Synthesis of Siloxanes Using Karstedt's Catalyst



Compounds **1**−**3** were synthesized via hydrosilylation reactions catalyzed by Karstedt's Pt^0-catalyst in dry toluene under argon at 70 °C (Scheme 1). The synthesis of starting material **4** and the final products **1**, **2**, and **3** is described in detail in the Supporting Information. Dimer **1** and tetramer **2** were obtained in a reasonable overall yield of around 50%, but pentamer **3** could only be obtained in a very low yield (~1.5%), which we attribute to the previously reported inaccessibility of the fifth hydrogen atom in the ring after the initial four substitutions.[10] Addition of more alkene and/or catalyst or increase of the reaction temperature did not help to drive the reaction further to completion.

Unlike compound **1**, compounds **2** and **3** display more than one signal for the naphthalene aromatic rings in ^1H NMR spectra (Figure 1a). Though the peak patterns of **2** and **3** might look like a multiplet because of its symmetrical nature, variation of the magnetic field strength (300 vs 400 MHz) revealed a field-dependent splitting between the peaks. As a result, the splitting patterns are not due to proton−proton coupling, but are caused by a set of stereoisomers that display singlet peaks with different chemical shifts from different aromatic rings.

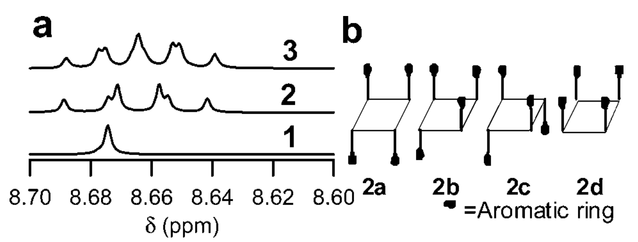


Figure 1. (a) ^1H NMR spectra of siloxanes in the aromatic region (300 MHz); (b) possible stereoisomers of **2**.

In the case of tetramer **2** four stereoisomers are possible (see Figure 1b) with a statistical distribution of 2:4:1:1. The observed ratios could be different from the statistical distribution, because of epimerization that allows equilibrium distributions.[11] The observance of six rather than of four peaks in the ^1H NMR spectrum can be explained by studying the environment of the NDI rings in isomers **2a**−**d**. In compounds **2a** every ring is oriented *cis* to one neighboring ring, and *trans* to the other, while it is oriented *trans* with respect to the aromatic ring across the siloxane ring. As a result all aromatic rings are in the same environment, and show up as one peak. Analogous arguments apply for **2c** and **2d**, which yield peaks at different δ-values than **2a** due to differences in the environment. However, the NDI rings in **2b** are not all identical, and show up as three singlets in a ratio of 1:2:1; given that **2b** amounts statistically to half of the distribution, 6 signals are to be expected in the ^1H NMR with a signal ratio of 1:1:2:2:1:1, as is experimentally observed. In fact, this is the first reported case in which the

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ratios match exactly the statistical distribution, since epimerization is blocked by the bulky substituents at the Si atom.[11a] Analogously, for pentamer **3** four stereoisomers are possible,[11b] giving rise to ten different environments for the NDI rings due to splitting of peaks of three isomers into a 2:2:1 ratio (see the Supporting Information). Since the addition of the fifth substituent is highly activated (vide supra), no statistical mixture is to be expected, in line with the observation of seven peaks in the ^{1}H NMR spectrum of **3** with an observed peak ratio (%) of 7.7:9.8:11.6:31.8:14.0:14.5:10.6.

Absorption spectra of **1**−**3** obtained at micromolar concentrations showed a normal absorption of NDI with vibrational features (Figure 2a).[6] For **1**, but not for **2** and **3**, an extra absorption band around 450 nm appears upon increasing the concentration to the millimolar range, which we attribute to ground state aggregation (Figure 2b). In contrast, the steady-state emission spectra of all three compounds displayed, over the whole measurable concentration range, two distinct features, namely, the monomer (410 nm) and exciplex (510 nm) emission. This kind of emission was observed even at submicromolar concentrations (10^{-7} M), indicating that the emission at 510 nm is due to intramolecular excimer formation.

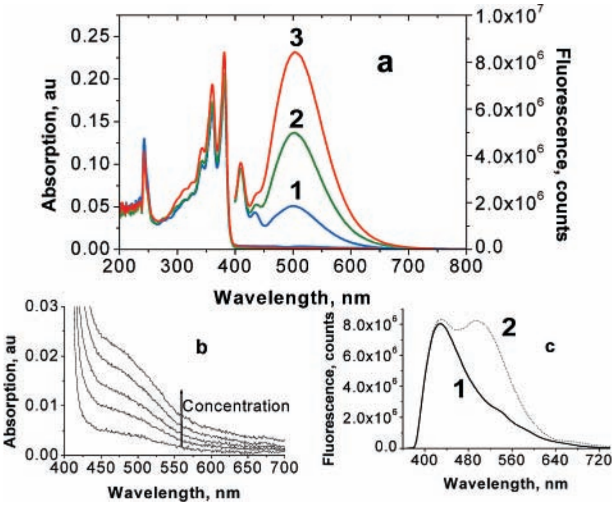

Figure 2. (a) Absorption and emission (λ_{exc} = 381 nm) spectra of dimer **1** (blue, 5.04 μM), tetramer **2** (green, 2.54 μM), and pentamer **3** (red, 1.96 μM) in $CHCl_3$; concentrations were chosen to yield equal chromophore concentrations. (b) Absorption spectra of dimer **1** at higher concentrations (2−10 mM). (c) Emission spectra of **1** (solid line) and **2** (dotted line) in ODCB (~8 μM).

The position and intensity of the fluorescence of **1**−**3** are significantly influenced by the solvent (Figure 2c). On going from chloroform to *o*-dichlorobenzene (ODCB), the monomer fluorescence of **2** enhanced with a shift from 410 to 430 nm, while the excimer fluorescence decreased in intensity. This phenomenon is attributed to $\pi-\pi$ stacking of the aromatic solvent with the chromophores,[12] which diminishes excimer formation for **2**. For low concentrations of compound **1** this $\pi-\pi$ stacking in ODCB even leads to disappearance of the excimer peak.

Nanosecond laser flash photolysis (LFP) studies on siloxanes **1**, **2**, and **3** in chloroform reveal the triplet spectrum of the NDI moieties (Figure 3).[6] Since the higher triplet states lie close to the excited singlet states, the intersystem crossing is very efficient and rapidly deactivates the excited singlet states. This leads to low fluorescence quantum yields and short singlet lifetimes.[13] These triplet spectra were vibrationally (456 and 485 nm) resolved up to a certain concentration. Above this concentration (for **1**, 0.1−0.2 mM; for **2**, 0.005−0.01 mM; for **3**, 0.008−0.01 mM) the spectra were red-shifted with loss of vibrational resolution. The red shift in the transient absorption maxima is more pronounced in dimer **1** (510 nm) than in **2** and **3** (505 nm). At these concentrations, an extra shoulder was seen in the UV−vis spectrum of **1** indicating the formation of ground-state aggregates as shown in Figure 2b. Such a shoulder was not seen in UV−vis spectra of **2** and **3**. However, for these compounds, it is also expected that intermolecular $\pi-\pi$ stacking of chromophores becomes more significant at higher concentrations, resulting in both changes in the vibrational features[14] and the red shift in the triplet absorption maxima. As this was indeed observed in pure films of both **1** and **2** (see the Supporting Information), we hypothesize that intermolecular complexes are ubiquitously present.

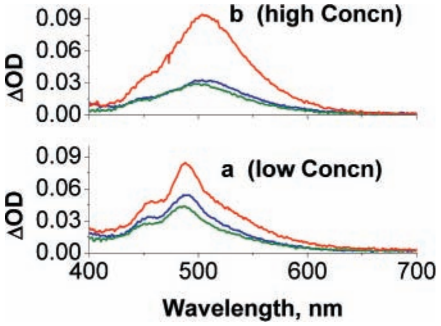

Figure 3. Transient absorption spectra of **1** (blue), **2** (green), and **3** (red) in chloroform: (a) at low concentration [**1**, 100 μM; **2**, 50 μM; and **3**, 20 μM] and (b) at higher concentration [**1**, 0.2 mM; **2**, 0.1 mM; and **3**, 79 μM (λ_{exc} = 355 nm; fwhm = 4 ns).

The presence of intermolecular complexes at higher concentrations was also confirmed by time-resolved nanosecond fluorescence spectroscopy. Immediately after the laser pulse, at low concentrations no excimer/exciplex peak was seen (4, 5, and 10 μM, for **3**, **2**, and **1**, respectively), whereas at 50-fold higher concentrations an excimer component was clearly observed (Figure 4; λ_{exc} = 355 nm; fwhm = 4 ns). Measurement of the fluorescence 6 ns after the pulse yields

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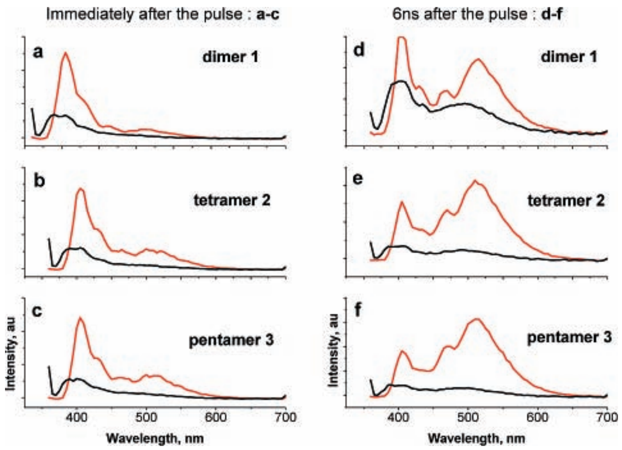

Figure 4. Time-resolved emission spectra of siloxanes in $CHCl_3$ at low (black line) (**1**, 10 μM; **2**, 5 μM; and **3**, 4 μM) and high (red line) (**1**, 0.5 mM; **2**, 0.25 mM; and **3**, 0.2 mM) concentrations, immediately (a−c) and 6 ns (d−f) after the pulse.

a clear excimer emission already at the lower concentrations. At higher concentrations, the chromophores form ground state dimers, which are excited and yield the exciplex emission immediately after the pulse. At lower concentrations the formation of ground state aggregates is less likely. Femtosecond transient absorption and picosecond fluorescence spectroscopies show the singlet lifetime of NDI to be ~10 ps.[13] This is confirmed by picosecond time-correlated single photon counting measurements (TCSPC) of **1**−**3** in chloroform, which show a multiexponential decay with lifetimes ranging from 13 ps to 18 ns (see the Supporting Information). The shortest observed lifetime is in line with the ~10 ps singlet lifetime of NDI. Therefore, excimer formation by diffusion also is not possible. Since NDIs form triplets efficiently, the excimer fluorescence is likely due to triplet−triplet annihilation, in which the diffused molecules stay together.[15] This also explains why the exciplex intensity increases over time from directly after the pulse to 6 ns thereafter.

Polarized optical microscopy shows that dropcasted neat films of **1**−**3** are amorphous, and this is also the case for films in which these siloxanes are mixed with well-known polymeric *p*-type materials such as poly(2-methoxy-5-{3′,7′-dimethyloctyloxy}-*p*-phenylene vinylene) [MDMO-PPV] and poly-(3-hexylthiophene) [P3HT]. Next, the fluorescence quenching of these *p*-type polymers was tested, both in solution and in films. Figure 5 shows the fluorescence quenching in a 1:1 (wt %) mixture of siloxanes **1**−**3** with MDMO-PPV and P3HT, respectively.

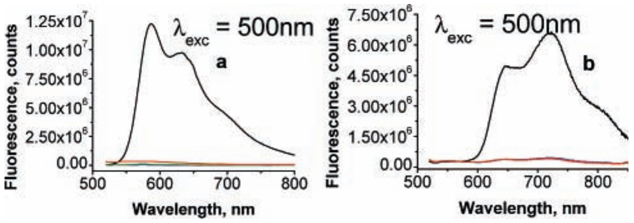

Figure 5. Fluorescence quenching of MDMO-PPV (a) and P3HT (b) by **1** (blue), **2** (green), and **3** (red) in 1:1 wt % films spin coated from *o*-dichlorobenzene at 2000 rpm for 60 s.

All three siloxanes **1**−**3** were very efficient in quenching the singlet excited states of the *p*-type materials. This indicates a highly efficient electron transfer from the *p*-type material to the NDI moieties. In fact, MDMO-PPV fluorescence was quenched by **1** and **2** (>99.9% in 1:1 films) even more efficiently than previously reported for the tetrahedral tetraphenylmethane derivative with NDI moieties,[6] which make them highly promising materials for further (photo-)-electrical studies. The quenching efficiencies of all three siloxanes were almost equal upon 1:1 (wt %) mixing with P3HT (Figure 5b). These quenching experiments in film with two different well-known donor polymers point to the versatility of these siloxanes.

In conclusion, we have synthesized new cyclic and amorphous siloxanes, which consist of sets of stereoisomers bearing electron-accepting NDI moieties. The size of these NDI moieties prevents the interconversion of these isomers, via, e.g., epimerization, which for the first time allows the use of cyclic siloxanes to obtain a stable and controllable morphology. Photophysical measurements display that intermolecular interactions of acceptor chromophores occur at higher concentrations. This opens up the possibility to create continuous pathways for charge transport in appropriate films, which is under current investigation. A major stimulus for such further studies is the highly efficient quenching of the fluorescence of various *p*-type polymers by the NDI moieties, which points to the potential of these amorphous siloxanes as *n*-type materials in applications such as organic solar cells.

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Supporting Information Available: Synthesis and NMR data of siloxanes **1**, **2**, and **3** and the starting alkene **4**, as well as TCSPC data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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