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Synthesis and Ultrafast Broadband Optical Limiting Properties of a Two-Branched Twistacene

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Abstract: A novel two-branched twistacene (PyDN) has been designed and synthesized for application on ultrafast optical limiting. This twistacene exhibits excellent two photon absorption and two photon absorption-induced excited singlet state absorption, which was systematically investigated with a femtosecond Z-scan experiment, transient absorption spectrum, and two-photon excited fluorescence experiments. The admirable two photon absorption is attributed to the high degree of π electron delocalization in twistacene which is caused by introduction of two strong donors. The excited singlet state absorption cooperates with two-photon absorption to provide an excellent ultrafast optical limiting behavior with high linear transmittance, where the thresholds are 2.3–5.3 mJ/cm² in the spectral region of 532–800 nm of femtosecond laser and 133 mJ/cm² for picosecond pulse at 532 nm. These thresholds are lower than that of most of the optical limiters reported previously, which indicates PyDN is a promising candidate for ultrafast optical limiting.

Keywords: twistacenes; optical limiting; two photon absorption; excited singlet state absorption

1. Introduction

With the advancement of advanced laser techniques, ultrafast lasers have been widely applied to various fields such as machining, energy conversion, imaging, communications, surgery, and medicine [1–3]. Developing optical limiting (OL) materials to protect human eyes and sensitive instruments from high-intensity ultrafast lasers damage is increasingly important. In recent years, great efforts have been devoted to various OL materials such as graphene families [4,5], nanomaterials [6,7], organic compounds [8,9], and so on [10]. Among them, organic π-conjugated compounds have received more attention due to their structural flexibility, the easy fabrication of devices and strong nonlinear optical absorption. For most OL materials, optical nonlinear response is based on nonlinear scattering or excited triplet state absorption of materials [11,12]. These materials are usually highly efficient for long laser pulses (nanoseconds), but are weak for ultrashort laser pulses (femtoseconds and picoseconds for examples). In this case, utilizing two-photon absorption (TPA) induced excited singlet state absorption to realize ultrafast broadband OL behavior is one feasible way to avoiding this disadvantage. Moreover, if the lifetime of the excited-state lifetime in these materials falls into the long pulse duration of the laser, an OL response for different laser pulses could be realized. The TPA is a broadband absorption behavior and can cover a wide spectral region from visible to near-infrared. Together with a broadband excited state absorption (ESA), OL performance will be significantly improved under the various wavelengths, which is a key factor to realize the broadband response to different input laser wavelengths. In addition, the zero contribution of one photon absorption in this
Twistacenes, as a member of polycyclic aromatic hydrocarbons (PAHs) families, contain rigid pyrene units and terminal linked acenes [17,18], which possess a very large π conjugated system and exhibit excellent electro-optical activity [19–22]. Interestingly, the formed twistacenes exhibit the excellent nonlinear absorption (NLA) properties, which are favorable for OL application, and have attracted our attention. Chen et al. found that end-modified unsymmetrical twistacenes possessed broadband excited state absorption behavior [23]. Then, Wu et al. reported a series of spindle-type conjugated twistacenes dimer, where the TPA-induced excited singlet state absorption of these twistacenes was investigated and confirmed. Moreover, extending the π-conjugated framework in these twistacenes can enlarge the ESA on singlet state, while it retains its broad excited-state absorption spectrum [24]. Song et al. reported a class of phenylacetylene-functionalized twistacenes and twistfuranacenes, and found that the two-photon absorption performance of materials was heavily dependent on the terminal substituted group. The triphenylamine decorated twistacenes exhibited enhanced two-photon absorption behavior, which was ascribed to the introduction of a strong donor into the twistacene unit, which efficiently improved the degree of delocalization of π electrons in twistacenes [25]. These observations inspired us to construct new twistacenes with strong a NLA ability for ultrafast OL application.

In this work, we designed and synthesized a novel twistacene (PyDN in Scheme 1), which contains of a twistacene unit and two strong donors (N,N-dimethylaniline), and systematically investigated the TPA and excited-state dynamics of PyDN with a femtosecond Z-scan experiment, transient absorption, and two-photon excited fluorescence experiments. Benefiting from the good overlap of TPA and ESA, PyDN exhibits excellent ultrafast broadband OL performance in femtoseconds and picoseconds regimes.

Scheme 1. Molecular structures of PyDN.

2. Results and Discussion
2.1. Molecular Design and Synthesis

Nonlinear optical properties of organic materials originate from the efficient delocalization of the π-electron. Extending π-conjugated frameworks of a system and introduction of donor or acceptor groups are well-known strategies to improve the NLA property of materials [16,26]. Previous reports showed that the introduction of a strong donor into the twistacene unit could efficiently enhance two-photon absorption capacity in one-branched twistacenes [25]. In addition, a multi-branched structure could provide a larger conjugate system than a one-branched structure, which is expected to improve the OL performance of materials [27,28]. Hence, we designed a two-branched twistacene structure by decorating the strong donor group (N,N-dimethylaniline) with acetylene bond as π bridge in adjacent position. This structure possesses an extended π-conjugated system and strong donor, which is expected to improve the OL performance of twistacene. A synthetic route to PyDN is depicted in Scheme 2. PyDN was prepared from disubstituted twistacene 1 and
4-ethynyl-N,N-dimethylaniline, catalyzed by Pd(PPh₃)₂Cl₂ via a Sonogashira reaction. PyDN was characterized by ¹H NMR, ¹³C NMR spectroscopy and mass spectroscopy (See the Supplementary Material).

Scheme 2. Synthetic route to PyDN.

2.2. Electronic Structure Analysis

To gain insight into the NLA properties of PyDN, theoretical calculations were conducted using a Gaussian 09 software package [29]. The ground states molecule were optimized using the B3LYP/6-31G(d,p) level of density functional theory (DFT), and the excitation energy was calculated by using the time-dependent density functional theory (TD-DFT) at same level. After that, the natural transition orbitals (NTOs) calculation was performed to describe the electronic structure characteristics on the excitation states. The calculated result is illustrated in Figure 1.

Figure 1. Optimized structure and the natural transition orbitals in the first excited state (S₁) of PyDN.

The optimized structures show these two modified groups are almost coplanar with the terminal acene structure of twistacene unit. Even though these two modified groups are decorated in adjacent positions of one benzene ring of a twistacene, the introduction of acetylene bonds as a π bridge results in almost no steric hindrance effect between both modified groups. This planar conformation does not cause the twisted intramolecular charge transfer, which is beneficial to the enhancement of TPA [30]. The result of NTOs shows that hole orbital is mainly localized on whole molecular skeleton including the twistacene unit and two modified groups, whereas the distribution of electron orbitals is more localized on the twistacene unit. These observations show that the absorption mainly originates from π→π* transitions, including a certain amount of π electron transfer from modified group to twistacene unit in the process of absorption. The distribution of hole orbitals indicates that the whole molecular skeleton participates in the NLA process, thus resulting in larger delocalization area, which is conducive to the enhancement of TPA. Moreover, transferring a certain amount of π electrons to a twistacene will activate the activity of twistacene with a large conjugated system, which is a benefit to π electron delocalization. Compared withs other twistacenes [23,25], the two-branched twistacene PyDN possess a higher degree of π electron delocalization, which is mainly caused by the extending conjugated plane of the system. To further research the substituent effects, a class of similar twistacenes are designed and calculated for comparison, and the calculated results are illustrated in Figure S2. The distributions of orbitals in these three twistacenes are
wider than their corresponding one-branched structures [25], indicating the two-branched architectures can provide more of an NLA response. An obvious charge separation in NTOs can be observed in the twistacene with strong acceptor moieties (4-nitrobenzene), which will provide a small distribution of delocalized π electrons and is unfavorable to the enhancement of NLA [30]. In addition, the charge transfer from substituent group to twistacene unit is enhanced by increasing the electron-donating ability of substituent groups, which will be better to activate the large conjugated twistacene units and cause a higher degree of π electrons delocalization. These results show that PyDN possesses a high degree of π electron delocalization, and thus, it could maybe provide excellent NLA [16,26].

2.3. UV-Vis Absorption and Emission

The UV-vis absorption and emission spectra of PyDN were investigated in toluene solution (1 × 10^{-5} M) at ambient condition. As shown in Figure 2, compounds of PyDN show obvious absorption in the spectral region of 300–481 nm with absorption bands at 342 nm, 359 nm, and 375 nm, which are assigned to the n–π* and π–π* transition of the skeleton. Compared with single modify group decorated twistacenes [25], there is a slight red shift, which is caused by the extending conjugated system. When excited at 359 nm, PyDN emitted light centered at 459 nm with quantum yields (ΦF) of 0.38, using 9,10-diphenylnanthracene (ΦF = 0.95 in ethanol) as a standard. The optical energy gaps (Eg) were calculated to be 2.60 eV, according to the absorption edges at 480 nm in toluene.

![Figure 2. UV-vis absorption (red line) and emission (blue dots) spectra of PyDN in toluene. Insets is photograph achieved under black back light with excitation at 365 nm in toluene.](image)

2.4. Open Aperture Z-scan and Transient Absorption Spectrum Experiments

NLA response of PyDN in toluene with a concentration of 2.4 × 10^{-3} M was investigated by an open aperture Z-scan experiment. Yb:KGW fiber laser equipment (Light Conversion, PHAROS-SP) with an optical parametric amplifier (OPA, Light Conversion), which delivers tunable wavelength with ~190 fs pulses, was used as a laser light source, where laser frequency was set at 20 Hz to exclude NLO response from thermal effect. The background signal of toluene solvent was tested to guarantee an NLA signal in the Z-scan that comes from PyDN. A broadband NLA is more favorable for the application of ultrafast OL, hence NLA capacity of PyDN was investigated in a wide optical window from 532 nm to 800 nm. The transmittance of the sample was recorded by a power meter, and the experimental data were shown in Figure 3a. PyDN possesses excellent reverse saturable absorption behavior in the wide spectral region, suggesting that PyDN is a good broadband optical limiting material. To investigate the mechanism of absorption, the open-aperture Z-scan experiments with different input intensities of laser beams were carried out at 532 nm and shown in Figure 3b.
carried out to investigate the dynamics of excited state in pump light was set to 400 nm to ensure that the sample can be efficiently excited. Moreover, different incident laser energies at 532 nm.

The different colored dots are the experimental data and solid lines represent the theoretical fitting.

The nonlinear absorption coefficient at can be calculated by using the following equation [31],

$$ T(z) = \sum_{m=0}^{\infty} \frac{[-\beta_{\text{eff}} I_{\text{eff}} / (1 + z^2 / z_0^2)]^m}{(m + 1)^3/2} $$

where $I$ is the input intensity of the laser beam, $\beta_{\text{eff}}$ is effective NLA coefficients, $a_0$ is the linear absorption coefficient, $L_{\text{eff}} = [1 - \exp(-a_0 L)] / a_0$ represents the sample thickness, and $z_0$ and $z$ represent the diffraction length of the beam and the propagation axis coordinate, respectively. The calculated $\beta_{\text{eff}}$ is nearly proportional, thus increasing the function of input intensity $I$ (Figure 3c), which indicates that there is not only mechanism of third-order nonlinear absorption but also a contribution from a higher-order nonlinear response. Considering the zero contribution from one-photon absorption under selected wavelengths, the absorption process of PyDN may be assigned to a two-photon (TPA)-induced excited state absorption [14,32]. As three photons are absorbed in the process, TPA-induced excited-state absorption is therefore an effective fifth-order nonlinear absorption.

To validate this absorption process, a femtosecond transient absorption experiment was carried out to investigate the dynamics of excited state in PyDN, and the wavelength of pump light was set to 400 nm to ensure that the sample can be efficiently excited. Moreover, the probe beam is the white light produced in a 2 mm thick Ti sapphire plate. As shown in Figure 4, PyDN exhibits a broadband excited state absorption (ESA) behavior (OD > 0) in a spectral region from 476 nm to 760 nm with a strong absorption peak at 662 nm. The negative signal centered at 458 nm is ascribed to the superposition of stimulated emission signal with ESA (Figure 2). During the entire delay time, the curve shape of ESA remains the same with a time depend decay of OD, indicating that the ESA originates from an excited singlet state and there is no additional transition process occurring [33–35]. This ESA behavior is appreciated in ultrafast OL.

The dynamics process can be well fitted throughout the global analysis and two processes were successfully extracted, with a fast process with a time constant of 0.38 ps and a slow process with a lifetime of 3.6 ns (selected dynamic traces and fitting process in Figure S1). Under photoexcitation, the whole transition process can be described as PyDN first being pumped to an excited state (S1) by absorbing a photon, then other photons are absorbed to transfer to a higher excited state (ESA process). After that, molecules in a higher excited state decay to S1 through the vibrational relaxation of the hot exciton with a lifetime of 0.38 ps, and finally back to the ground state with a lifetime of 3.6 ns. To further validate the process, a transient fluorescence experiment of PyDN in toluene was performed. The dynamic curve of fluorescence can be well-fitted by using a mono-exponential function with a lifetime of 3.5 ns (Figure S3), which is in good agreement with the fluorescence lifetime from a single-exponential function with a lifetime of 3.6 ns.
agreement with the long lifetime in TAS. This result provides more proof to excited singlet state absorption.

\[ α = α_0 + βI + γI^2 \]  

(2)

where β and γ represent the TPA coefficient and three-photon absorption coefficient (TPA-ESA absorption), respectively. Additionally, the TPA cross-sections can be calculated by using the equation: \[ σ_{TPA} = \hbar ωβ/N, \] where \( h\omega \) represents the photon energy at the selected wavelength and \( N \) is the number density of PyDN in toluene. The TPA cross-sections and three-photon absorption coefficient at the selected wavelengths can be obtained by fitting the open-aperture Z-scan data using Equations (1) and (2) again. As shown in Table 1, DyPN exhibits good two-photon absorption behavior with a maximum absorption cross-section of 2476 GM.

**Table 1.** The parameters of TPA and TPA induced ESA of PyDN under selected wavelengths achieved from Z-scan measurements.

|          | 532 nm | 600 nm | 700 nm | 800 nm |
|----------|--------|--------|--------|--------|
| \( β \) [10^{-2} \text{cmGW}^{-1}] | 9.57   | 5.00   | 1.41   | 0.54   |
| \( σ_{TPA} \) [GM]               | 2476   | 1147   | 277    | 93     |
| \( γ \) [10^{-4} \text{cm}^3\text{GW}^{-2}] | 6.50   | 2.98   | 2.13   | 1.21   |

2.5. Two-Photon-Excited Fluorescence (TPEF) Experiment

To further investigate the TPA behavior of PyDN, the two-photon-excited fluorescence (TPEF) experiment was conducted. PyDN was freshly dissolved in toluene with a concentration of \( 1 \times 10^{-4} \text{M} \) for this measurement. The laser source is same with the z-scan experiment, and the repetition rate is set at 6 kHz. The intensity level of the laser beam was carefully controlled to prevent saturation of absorption and photodegradation of PyDN in the process of measurement. The excitation wavelength of this measurement was selected in spectral region from 610 nm to 900 nm, as the shorter wavelengths will interfere with the collection of the fluorescence signals, resulting in large discrepancies between the
experimental results and real results in our measurement system. PyDN exhibits bright and observable emissions by an unfocused femtosecond laser beam at selected wavelengths (Figure 5a). The intensity of emission shows obvious power-squared dependence on the input excitation intensity under selected wavelength, which confirms that the observed fluorescence emission at a selected wavelength is mainly induced by TPA rather than another absorption process (Figure 5b). In addition, the shape and position of fluorescence emission is identical to the one photon excited fluorescence band, which indicates that the final excited states of TPA is the same as that of one photon absorption, and that no excitation process participates in the TPA-induced fluorescence emission.

![Normalized two-photon-excited emission spectra in toluene](image)

**Figure 5.** (a) Normalized two-photon-excited emission spectra in toluene; (b) the logarithmic plots of power-squared dependence of two-photon-excited fluorescence intensity on the laser intensity.

The TPA cross-sections of PyDN were obtained by using fluorescein in water at pH 11 as a standard, and were calculated using the following equation [37]:

\[
\delta_s = \frac{S_s C_s \Phi_s \eta_s}{S_r C_r \Phi_r \eta_r} \cdot \delta_r
\]

(3)

where \(s\) and \(r\) represent the measured sample and reference sample, respectively. \(S\) is the detected fluorescence integral area, \(C\) is the concentration of the sample, \(\Phi\) represents the fluorescence quantum yield of sample, \(\eta\) represents the collection efficiency of the experimental instruments. The PyDN sample and the reference sample were placed into a 10 mm spectroscopic quartz cuvette, and every measurement for these two samples was conducted under the same experimental conditions. The obtained TPA spectra (Figure 6) agrees with that of one photon absorption, which confirms that the transition of TPA is the same as that of one photon absorption (S0–S1 transition). The maximum value of the TPA cross-section is 1620 GM at 610 nm, which is larger than the corresponding value from Z-scan experiment at same wavelength. This observation may be resulted from the partial bleaching of high concentration samples used in Z-scan experiment [38]. Compared with single modify group decorated twistacenes [25], the TPA cross-section of PyDN from both methods was been greatly improved, which may have been caused by extending the conjugate system introduced by the strong donor decorated two-branched structure.
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2.6. Ultrafast Optical Limiting

It is well known that an ideal optical limiting device is expected to possess some characteristics, including high linear transmittance, strong reverse saturated absorption ability, temporally agile response to incident laser pulses, and a broadband response to various wavelengths. Among various NLO mechanisms employed for OL, TPA is a most promising process to meet these requirements, where a zero contribution of linear absorption will make materials transparent to the incident laser pulse under a low intensity, and the quadratic dependence on the input laser intensity can produce good reverse saturated absorption behavior. In addition, an outstanding overlap between the TPA and excited state absorption can efficiently improve the reverse saturated absorption ability of materials to achieve better control to high intensity laser. Under these considerations, PyDN possesses the TPA and TPA-induced excited state absorption properties which are excellent candidates for application on ultrafast broadband OLs.

The OL behavior of an organic solution depends on both the reverse saturated absorption ability of materials and the concentration of organic compounds in a solution. Hence, a nearly saturated PyDN solution in toluene was prepared to evaluate the OL performance. The apparatus for OL measurement was similar to the open-aperture Z-scan experiment, where a computer-controlled energy flow modulator consisting of a half wave plate and a linear polarizer was added to modulate the incidental energy flow of the sample. A PyDN solution in a 5 mm spectroscopic quartz cuvette was placed in front of lens. Femtosecond laser pulses with wavelengths at 532 nm, 600 nm, and 800 nm were employed to characterize TPA-based optical power that was suppressing properties of PyDN. Although the OL performance in femtosecond regime has been mentioned in terms of the open aperture Z-scan experiment, the detailed limiting threshold has not been discussed. The result is illustrated in Figure 7.

Obviously, high transmittance at low incident energy (T > 90%) quickly decreases with the increasing of incident laser fluence, indicating an effective suppression of a high intensity laser pulse. The limiting threshold (F_{th}, defined as the incident fluence where the true transmittance reduces to half of the linear transmittance) is estimated to be 2.3 mJ/cm² (532 nm), 3.2 mJ/cm² (600 nm), and 5.3 mJ/cm² (800 nm). In addition, PyDN exhibits an excited singlet state absorption behavior, which breaks the limit of intersystem crossing for application on ultrafast OLs. The optical-power restriction behavior under the irradiation of picosecond laser pulses was also measured and investigated by employing a mode-locked Nd:YAG laser (15 ps) with a repetition rate of 10 Hz. As shown in Figure 7b, PyDN also exhibits an excellent OL performance with the picosecond pulse, and the threshold is estimated to be 133 mJ/cm². The ultrafast optical–control performance of PyDN under

Figure 6. TPA spectra in toluene measured by TPEE method.

![TPA spectra in toluene measured by TPEE method.](image-url)
femtosecond and picosecond laser pulses is comparable, or better than, previously reported graphene oxides [39], semiconductors [40], pyrene-based molecules [41], and hydrazine derivatives [15], indicating that twistacene derivatives are excellent candidates for ultrafast OL applications.

![Figure 7](image)

**Figure 7.** (a) Optical limiting behavior of PyDN under selected wavelength with a 190 fs pulse; (b) optical limiting behavior under 532 nm with a 15 ps pulse.

### 3. Materials and Methods

#### 3.1. General Method

Materials used in this paper were purchased from commercial companies. Dry triethylamine was obtained by distilling over calcium hydride (CaH₂). Tetrahydrofuran was distilled over sodium-benzophenone ketyl. ¹H NMR and ¹³C NMR spectra were recorded in 400 MHz for ¹H and 100 MHz for ¹³C at room temperature. UV-vis spectra were obtained using SPECORD 210 plus spectrophotometer. Fluorescence spectra were finished by using HITACHI (F-7000) spectrofluorimeter.

#### 3.2. Synthesis

A mixture of compound 1 (145 mg, 0.2 mmol), 4-ethynyl-Ν,N-dimethylaniline (70 mg, 0.48 mmol, 2.4 equiv), triphenylphosphine (5.6 mg, 0.024 mmol), CuI (4.5 mg, 0.024 mmol) and Pd(PPh₃)₂Cl₂ (14 mg, 0.02 mmol) in a Et₃N/THF (15 mL/5 mL, v/v = 1:1) was stirred for 16 h at 80 °C under a nitrogen atmosphere. After cooling to room temperature, brine was added and extracted with dichloromethane. The organic layers were collected, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was purified on silica gel column to afford a yellow solid compound PyDN (116 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ = 7.99–7.98 (d, J = 1.2 Hz, 1H), 7.93–7.87 (s, 7H), 7.70–7.68 (d, J = 7.2 Hz, 2H), 7.63–7.56 (m, 4H), 7.53–7.38 (m, 4H), 7.37–7.24 (m, 1H), 6.73–6.71 (d, J = 8.8 Hz, 2H), 6.60–6.58 (d, J = 8.8 Hz, 2H), 3.05 (s, 6H), 3.00 (s, 6H), 1.16 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ = 150.16, 149.57, 147.34, 147.00, 142.31, 141.85, 136.58, 136.01, 135.40, 133.35, 133.03, 132.86, 132.81, 132.62, 130.72, 130.70, 130.21, 129.53, 129.37, 129.31, 129.19, 128.76, 128.40, 127.74, 127.60, 127.42, 126.96, 126.74, 124.17, 123.85, 122.40, 122.17, 120.68, 111.85, 111.31, 110.00, 100.85, 91.97, 87.77, 87.36, 40.25, 34.73, 31.43. MS (MALDI-TOF, m/z): calculated for C₆₁H₅₆N₂, 853.14; Found, 853.17.

### 4. Conclusions

In summary, we have successfully designed and synthesized a two-branched decorated twistacene PyDN, and systematically investigated the nonlinear optical properties. The introduction of two strong donors into a twistacene effectively extends the π-conjugated plane and the degree of π electron delocalization, causing excellent nonlinear optical absorption behavior. The absorption mechanism based on TPA and TPA-induced excited singlet
state absorption is confirmed by the femtosecond Z-scan experiment, transient absorption, and two-photon excited fluorescence experiments. Benefiting from the spectral overlap between two photon absorption and the excited singlet state absorption, PyDN exhibits admirable ultrafast broadband OL performance in femtosecond and picosecond regimes with high transmittance and low thresholds, which is a promising candidate for ultrafast OL applications. In addition, the strategy of constructing twistacene by the introduction of multiple donors is very efficient route to improve the OL performance of materials, and it inspired us to construct new twistacenes for ultrafast OL applications in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27113564/s1, Figure S1: Dynamics traces of PyDN at 458 nm and 662 nm. The dots represent the experimental data and solid lines were theoretical fitted curves by global analysis; Figure S2: The natural transition orbitals in the first excited state (S1) of designed twistacenes; Figure S3: The emission spectra of PyDN in toluene under different incident laser energies at 400 nm. Insets is that linear dependence of one-photon-excited fluorescence intensity on the laser in-tensity; Figure S4: Fluorescence decay of PyDN in toluene. The solid line was fitted lifetime of 3.5 ns; Figure S5: 1H NMR spectrum of PyDN; Figure S6: 13C NMR spectrum of PyDN; Figure S7: MALDI-TOF spectrum of PyDN.

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Sample Availability: Samples of the PyDN are available from the authors.

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