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Synthesis of double-conjugated-segment molecules and their application as ultra-broad two-photon-absorption optical limiters

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A series of novel double-conjugated-segment molecules, in which two conjugated segments are separated by an ether chain, were synthesized; these compounds provide a very broad two-photon absorption spectral range, which satisfies an urgent need in the optical limiting area.

In recent years, organic molecules exhibiting strong nonlinear-optical behavior have received considerable interest because of their applicability in a variety of optical devices.[1–7] In particular, optical limiters have received attention as a result of a growing need for eye and optical sensor protection.[8] Two-photon-absorption (TPA, third-order nonlinear optical mechanism) optical limiters, which offer the advantage of a high transmission for the laser light with a frequency well below the bandgap frequency at low incident intensity, will absorb the light and decrease the transmission based on a two-photon-resonance process when the incident intensity is high.[9]

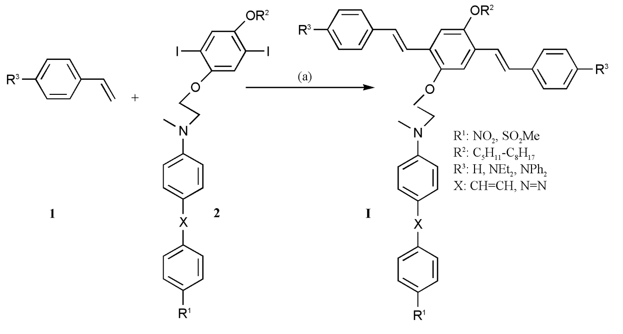
Because of the existence of lasers with different wavelengths in a wide spectral range, a broadband absorption nonlinear molecule is practically needed.[8] However, in traditional nonlinear absorption molecules with a single-conjugated segment, the primary absorption coverage derived from the electron transition from π orbit to π^* orbit is restricted to a narrow band. One way to broaden the absorption coverage is to blend different nonlinear molecules together. The absorptivity of the mixture has been found to be a linear sum of those of each compound.[10] But phase-separation will be a fatal problem in the practical application.

Recently in our laboratory, we were developing a new synthetic strategy, which combined two TPA conjugated segments in one molecule with a non-conjugated ether chain. We observed the broad linear absorption band and the broadband nonlinear absorption coverage arose from the π–π^* transition of those two conjugated segments. To the best of our knowledge, this is the first experimental realization of broadband two-photon optical limiters in one compound. In this communication, we report the synthesis of these double-conjugated-segment molecules and their application as broadband two-photon-absorption optical limiters.

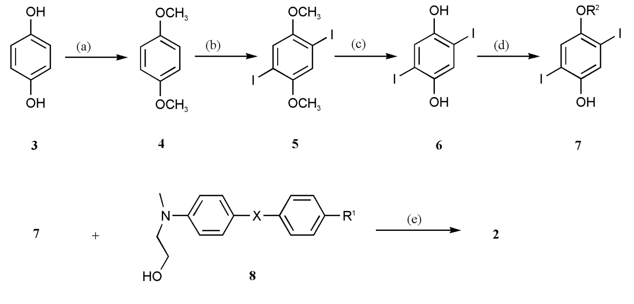
We have synthesized the double-conjugated-segment molecules **I** by reaction of diiodo compounds **2** with substituted styrene derivatives **1** in the presence of a catalytic amount of Pd (OAc)$_2$ and tri-*o*-tolylphospine (Scheme 1).† Compounds **I** contain an alkyl substituent R^2 which was introduced to increase the solubility of the resulting molecules. These molecules are soluble in CHCl$_3$, DMF, THF, tetrachloroethane, and so on. While R^2 was substituted by a methyl group, however, the resulting molecules cannot dissolve in common solvents except for NMP. The different conjugated bridges X (C=C and N=N) were chosen to alter the charge transfer characteristics and the molecule fundamental optical frequency. The functional groups R^1 and R^3 linked to the π-conjugated systems can increase the charge transfer ability in each conjugated chain, so as to enhance the molecule third-order nonlinearity. Moreover, those functional groups can also adjust the absorption wavelength. In our targeted molecules **I**, there are two separated conjugated segments. One is a donor–bridge–donor system; the other is a donor–bridge–acceptor system. These systems efficiently provide a large third nonlinear effect.

The diiodo compounds **2** were synthesized using the approach outlined in Scheme 2.† Methylation of hydroquinone **3** with dimethyl sulfate gave the corresponding bis-methyl ether **4** (82%). After iodination with I$_2$ (**4**→**5**, I$_2$, HIO$_3$, H$_2$SO$_4$, AcOH, 85%), demethylation (**5**→**6**, BBr$_3$, -78 °C to room temperature, 90%) was then achieved on treatment with BBr$_3$. A single alkyl substituent (**6**→**7**, R^{2}Br, KOH, DMSO, 56%) was introduced by controlling the amount of R^{2}Br added. The diiodo compounds **2** were synthesized by dehydration of **7** with **8** (containing one conjugated segment) under Mitsunobu reaction conditions using Ph$_3$P and diethyl azodicarboxylate (DEAD).

The measured linear absorption (LA) spectra of molecules **I** were found to be the mixture of the absorption bands of the two separated conjugated segments. Their absorption spectra contain two peaks or one peak and one shoulder instead. Each of these peaks corresponds to the fundamental frequency of each conjugated segment in comparison with that of the single conjugated molecule. For instance, the LA spectrum of **If** is shown in the inset to Fig. 1. The full width of the half maximum (FWHM) of each peak of **I** was selected as the parameter to describe the absorption range (Table 1). From Table 1, one can see that the absorption ranges are red-shifted with the increasing electron-donor ability of R^3 (H→NEt$_2$→NPh$_2$) or electron-acceptor strength of R^1 (SO$_2$Me→NO$_2$). Moreover, when the



Scheme 1 (a) Pd (OAc)$_2$, tri-(*O*-tolyl)phosphine, Et$_3$N.



Scheme 2 (a) (CH$_3$)$_2$SO$_4$, KOH, water, < 40 °C for 2 h, then reflux for 0.5 h, 82%; (b) I$_2$, HIO$_3$, H$_2$SO$_4$, AcOH, CCl$_4$, 75 °C for 3 h, 85%; (c) BBr$_3$, CH$_2$Cl$_2$, -78 °C to room temperature, 5 h, 90%; (d) R^{2}Br, KOH, DMSO, room temperature for 20 h, 56%; (e) DEAD, Ph$_3$P, THF, room temperature for 48 h.

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Table 1 Heck reaction yield, linear absorption range, nonlinear absorption range and effective nonlinear absorption cross-section of **Ia**–**Il**, in which the alkyl substituent R^2 is C_6H_{13}

Entry[a]	R^3	R^1	X	Heck reaction yield (%)	Linear absorption (LA) range/nm[b]	Nonlinear absorption (NLA) range/nm[bc]	Effective nonlinear absorption cross section/ cm^4 s photon^{-1}[d]
Ia	H	NO_2	C=C	80	350–485	670–970	10^{-47}–10^{-46}
Ib	H	NO_2	N=N	85	350–525	630–970	10^{-47}–10^{-46}
Ic	H	SO_2Me	C=C	84	345–450	—	—
Id	H	SO_2Me	N=N	88	348–502	—	—
Ie	NEt_2	NO_2	C=C	65	390–470	620–950	10^{-47}–10^{-45}
If	NEt_2	NO_2	N=N	67	392–518	720–1020	10^{-47}–10^{-46}
Ig	NEt_2	SO_2Me	C=C	50	400–454	—	—
Ih	NEt_2	SO_2Me	N=N	58	394–498	—	—
Ii	NPh_2	NO_2	C=C	32	420–487	—	—
Ij	NPh_2	NO_2	N=N	39	418–530	—	—
Ik	NPh_2	SO_2Me	C=C	30	415–458	—	—
Il	NPh_2	SO_2Me	N=N	44	421–500	—	—

[a] All compounds were characterized by MS, ^{1}H NMR† and EA. [b] The absorption range here is defined as the full width of half maximum (FWHM) of each peak. [c] The nonlinear absorption ranges were measured by direct nonlinear optical transmission. [d] The effective nonlinear absorption cross section were deduced from $T = \exp(-\alpha z)/(1+ (\beta/\alpha)I_0-(\beta/\alpha)I_0\exp(-\alpha z))$.

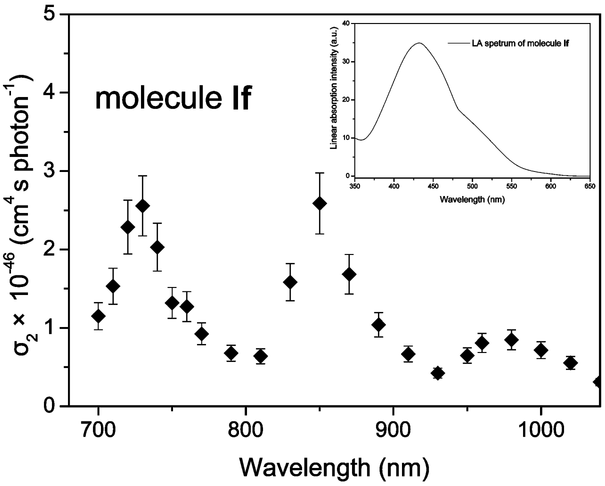

Fig. 1 Two-photon-absorption spectrum of **If**. The precision of our apparatus is about ±15%. The inset shows the LA spectrum of **If**.

conjugated bridge C=C was replaced by a N=N chain the linear absorption range was also red-shifted.

Two-photon absorption spectra of these compounds were measured by direct nonlinear optical transmission (NLT). The FWHM of their two-photon absorption spectra are also presented in Table 1. Here, only data for four compounds are shown for apparatus reasons. Extraordinarily broad spectral ranges were provided by compounds **I**, *i.e.* the nonlinear absorption (NLA) range of **If** is about 300 nm wide (Fig. 1). The NLA ranges of **I** are approximately two times the LA range. The effective nonlinear absorption cross section is of the order of magnitude 10^{-47}–10^{-46} cm^4 s photon^{-1}.

In summary, a new synthetic strategy was developed to synthesize a series of double-conjugated-segment molecules, which provided a very broadband two-photon absorption range. The optical limiters based on these novel molecules are promising in the near-infrared region.

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Notes and references

† Example of the Mitsunobu reaction (**2e**): diethylazodicarboxylate (DEAD) (1.00 g, 5.7 mmol) in THF (5 mL) was added into a solution of compound **7** (R^2=C_6H_{13}, 1.69 g, 3.8 mmol), 4-(2-hydroxyethyl)methylamino-4′-nitrostilbene (**8e**, 1.13 g, 3.8 mmol) and triphenylphosphine (1.50 g, 5.7 mmol) in THF (15 mL). The resulting solution was stirred overnight and then poured into hot methanol and filtered while it was still hot. The resulting red solid was purified by chromatography (CH_2Cl_2 as eluent) (2.18 g, 79%, mp 159–161 °C). ^{1}H NMR ($CDCl_3$, ppm): *d* 0.93 (m, 3H, $-CH_3$ in alkoxy), 1.36–1.86 (m, 8H, aliphatic protons), 3.22 (s, 3H, $-NCH_3$), 3.88 (t, *J* = 5.80 Hz, 2H, $-OCH_2CH_2N-$), 3.92 (m, 2H, $-OCH_2-$ on alkoxy side chain), 4.14 (t, *J* = 5.91 Hz, 2H, $-OCH_2CH_2N-$), 6.81 (d, *J* = 8.12 Hz, 2H, aromatic protons), 6.95 (d, *J* = 16.23 Hz, 1H, vinyl proton), 7.16 (m, 2H, aromatic protons), 7.19 (d, *J* = 16.33 Hz, 1H, vinyl photon), 7.25 (d, *J* = 8.26 Hz, 2H, aromatic protons), 7.58 (d, *J* = 8.42 Hz, 2H, aromatic protons), 8.19 (d, *J* = 8.64 Hz, 2H, aromatic protons). Anal. Calc. For $C_{29}H_{32}N_2O_4I_2$: C, 47.93; H, 4.41; N, 3.86. Found: C, 47.97; H, 4.50; N, 3.76%.

Example of the Heck reaction (**Ie**): triethylamine (0.24 mL, 1.72 mmol) was added to a solution of **2e** (0.5000 g, 0.689 mmol), *p-N,N*-diethylaminostyrene (0.2412 g, 1.378 mmol), $Pd(OAc)_2$ (6.2 mg, 0.0276 mmol), and tri-*o*-tolylphospine (42.0 mg, 0.138 mmol) in 10 mL of DMF. The resulting mixture was stirred at 80 °C overnight in a nitrogen atmosphere and was then poured into methanol. The precipitated solid was collected by filtration, then redissolved in tetrachloroethane and reprecipitated in methanol. The resulting dark solid was purified by chromatography ($CHCl_3$: cyclohexane = 20 : 1 as eluent) and then recrystallized from THF–hexane (0.367 g, 65%, mp 172–174 °C). ^{1}H NMR ($CDCl_3$, ppm): *d* 0.95 (t, 3H, $-CH_3$ in alkoxy), 1.15–1.17 (m, 12H, $-NCH_2CH_3$), 1.40–1.89 (m, 8H, aliphatic proton), 3.17 (s, 3H, $-NCH_3$), 3.17–3.36 (m, 8H, $-CH_2CH_3$), 3.85 (t, *J* = 5.45 Hz, 2H, $-OCH_2CH_2N-$), 3.90 (m, 2H, $-OCH_2-$), 4.28 (m, 2H, $-OCH_2CH_2N-$), 6.70 (d, *J* = 8.60 Hz, 2H, aromatic protons), 6.75 (d, *J* = 16.38 Hz, 1H, vinyl proton), 7.10 (d, *J* = 16.33Hz, 1H, vinyl proton), 7.14 (d, *J* = 6.40 Hz, 2H, aromatic protons), 7.18 (d, *J* = 15.80 Hz, 2H, vinyl protons), 7.23 (d, *J* = 7.82 Hz, 2H, aromatic protons), 7.26 (m, 2H, aromatic protons), 7.30 (d, *J* = 16.01 Hz, 1H, vinyl proton), 7.34 (d, *J* = 7.92, 2H, aromatic protons), 7.46 (d, *J* = 8.55 Hz, 2H, aromatic protons), 7.48 (s, *J* = 7.68Hz, 2H, aromatic protons), 7.52 (d, *J* = 7.45 Hz, 2H, aromatic protons), 7.56 (d, *J* = 16.55 Hz, vinyl proton), 7.88 (d, *J* = 8.00Hz, 2H, aromatic protons). Anal. Calc. For $C_{53}H_{64}N_4O_4$: C, 77.56; H, 7.80; N, 6.83. Found: C, 77.91; H, 7.51; N, 7.11%.

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