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Heterophenes revisited*

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Abstract: By employing the furan annulation protocol, a new series of furan-containing teraryl [n.2]cyclophenes (n = 2–6 and 12) are prepared. These cyclophenes exhibit charge-transfer character in the absorption spectra and unusually large Stokes shifts in the emission spectra. They have neither particularly strong electron-donating moieties nor electron-withdrawing groups, but exhibit unusual second-order nonlinear optical (NLO) properties. The π-systems in teraryl system and in the bridging double bond are highly twisted. Interaction between these twisted π-systems may account for the significant enhancement in hyperpolarizability. Thiophene analog behaved similarly. The five-membered heteroaromatic rings may not only serve as electron donors, but also may accommodate the appropriate geometry to enable the interactions between the oligoaryl systems and the double bond leading to unusual photophysical and NLO properties.

Keywords: cyclophenes; bridging double bond; furan-containing oligoaryls; twisted π-system; nonlinear optical properties.

INTRODUCTION

There has been increasing interest in the chemistry and applications of cyclophanes [1–3]. Incorporation of heteroaromatic ring(s) into cyclophanes apparently enriches the versatility of this class of molecules [4]. It is known that five-membered heterocycles such as furan, pyrrole, and thiophene are π-excessive, whereas the six-membered analogs such as pyridine and pyridazine are π-deficient. Indeed, the Hammet σ_p^+-values for 2-furyl and 2-thienyl moieties are –0.39 and –0.43, respectively, and σ_p^- for 2-pyridyl value is 0.55 [5]. Relatively speaking, the corresponding heterophenes constituting bridged double bond(s) have been only sporadically explored [6–11]. The first heterophene, [2.2](2,6)pyridinophane-1,9-diene **1**, was reported in 1970 [6]. Subsequently, several related compounds were synthesized [7–10]. To our surprise, only one mononuclear furan-containing [2.2]cyclophene **2** is reported in the literature as a side-product from a synthesis of furan-containing multiheteromacrocycle [11]. On the other hand, when a five-membered heteroaromatic ring is a part of an oligoaryl moiety, the use of a double bond as a bridge to link two oligoaryl chains is well documented [12–15]. Although these compounds are structurally similar to those of heterophenes, molecules like porphycenes **3** [13] and related compounds [13,14] are essentially planar owing to the geometrical requisite of five-membered heteroaromatic rings and therefore are considered as annulenes [12–15]. In this account, we summarize our recent studies on oligoaryl-cyclophenes **4** and related compounds which exhibit extraordinary photophysical properties and second-order nonlinear optical (NLO) properties.

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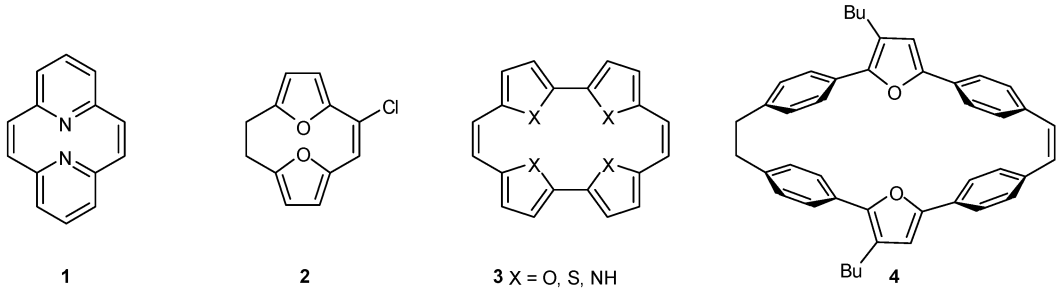
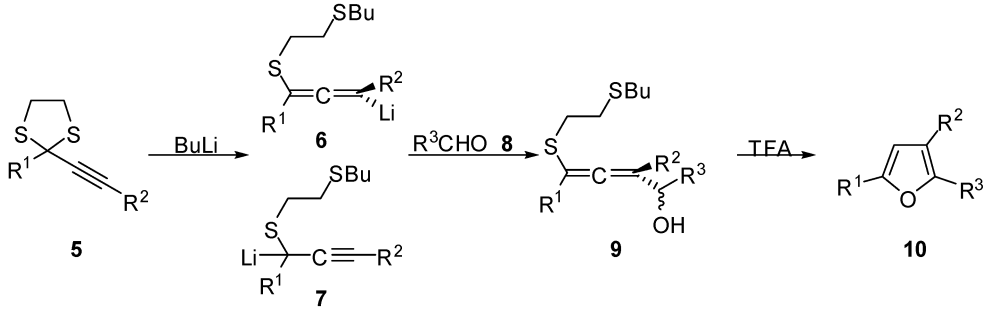


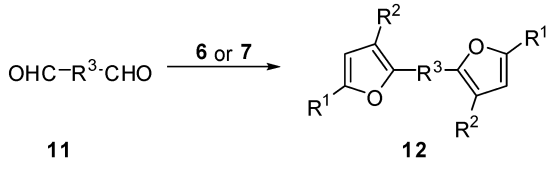
FURAN ANNULATION PROTOCOL

We began our research on oligoaryl-containing heterophanes by employing our new protocols for furan and pyrrole annulations [16–21]. Thus, when the propargylic dithioacetal **5** is treated with BuLi or organocuprate reagent, the nucleophile selectively attacks the sulfur atom of the propargylic dithioacetal, leading to the corresponding allenyl anion **6** or propargylic anion **7**. Reaction of **6** or **7** with an aldehyde **8** yields selectively the corresponding allenylcarbinol **9**, which is cyclized upon treatment with trifluoroacetic acid (TFA) to give furan **10** (Scheme 1) [18]. This procedure provides a useful entry toward the synthesis of furan-containing teraryls (**10**, $R^1 = R^3 = Ar$) when appropriate substrates **5** and **8** are used.

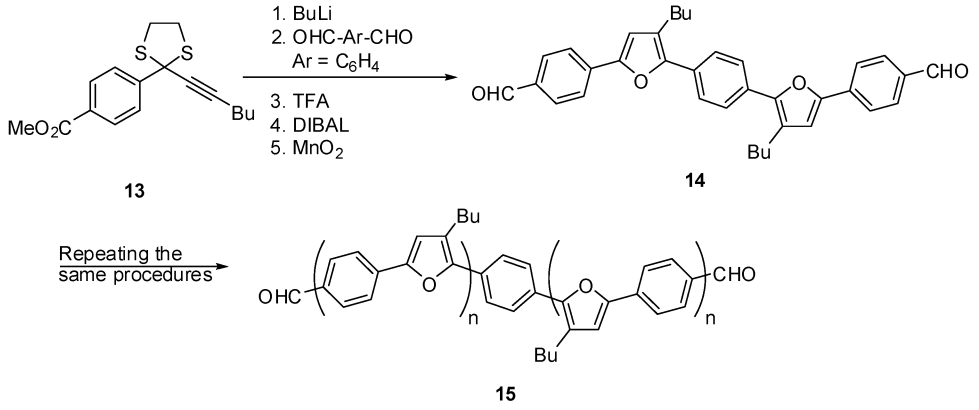


Scheme 1

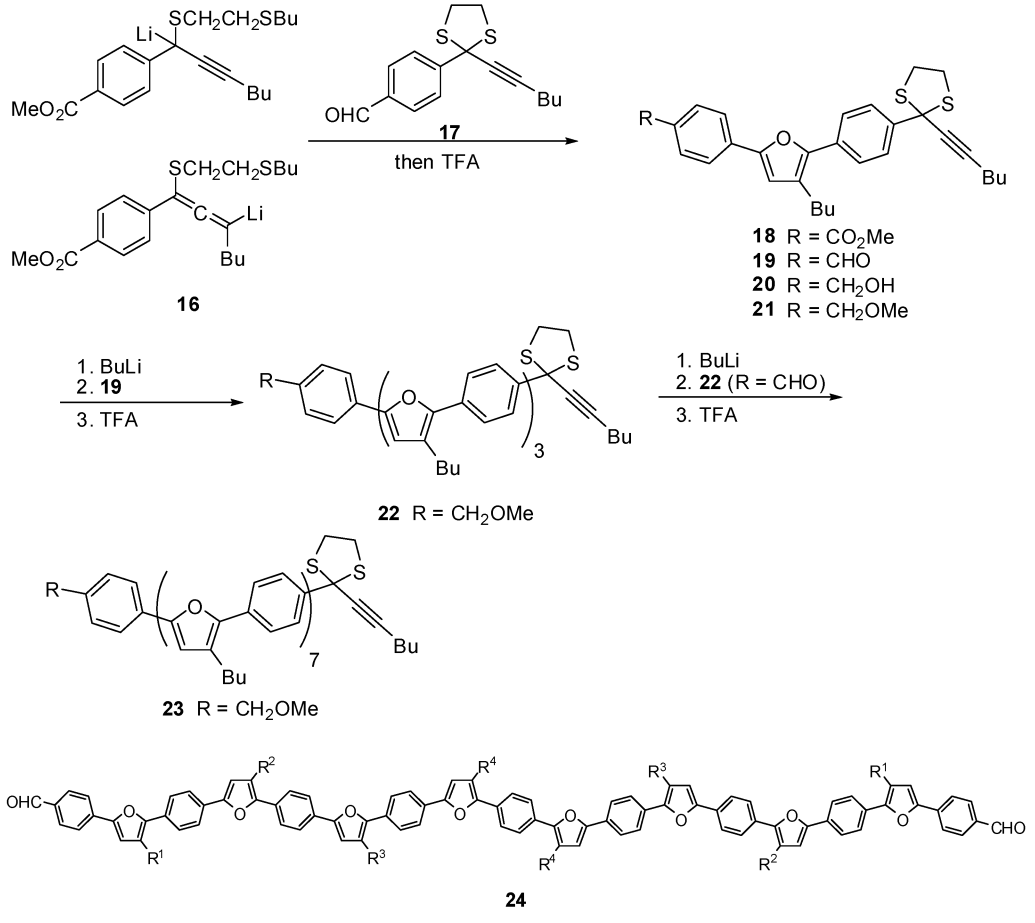
When a dialdehyde **11** is used, bis-furan product **12** is obtained in good yield (eq. 1). Functional groups such as esters are stable under the reaction conditions. Accordingly, bidirectional iterative protocol (Scheme 2) [19] and convergent strategy (Scheme 3) [20] have been developed for the synthesis of alternating benzene-furan oligomers, oligoaryl up to 17 nm lengths having been synthesized. This strategy can also be used for the synthesis of furan-containing oligoaryls **24** without repeating unit [20].



(1)



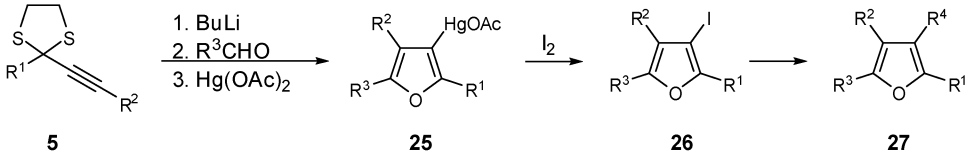
Scheme 2



Scheme 3

The aforementioned protocol is a general method for the synthesis of a range of tri-substituted furans. By simply modifying the procedure using mercuric acetate for the annulation step, the corresponding mercury-substituted furan **25** is obtained. Further reaction with iodine affords the corresponding

iodo-substituted furan **26**, which can be transformed into tetra-substituted furans **27** by cross-coupling reaction (Scheme 4) [21].



Scheme 4

FURAN-CONTAINING OLIGOARYLS AS HOLE-TRANSPORTING MATERIALS

Alternating benzene-furan oligoaryls are highly fluorescent with high quantum yield [18–20,22,23]. It is known that furan compounds are light-sensitive and can easily be oxidized by singlet oxygen. Accordingly, furan derivatives have rarely been used for materials applications [24]. On the other hand, in the absence of air, a thin film of furan-containing oligoaryls such as **28** remain intact upon irradiation with a sunlamp for 24 h. Recently, **28** was found to be a highly efficient hole-transporting material in an electroluminescent device, and the hole mobility of **28** is comparable with that of α-NPD **29** [22,23].

It is noteworthy that **28** undergoes revesible one-electron redox process and the corresponding blue-colored radical cation **30** has been dectected by absorption (Fig. 1) and electron spin resonance (ESR) spectra [25]. The same radical cation is also obtained by the treatment of **28** with concentrated sulfuric acid [25]. The high stability of the radical cation **30** may facilitate the electron-transfer process, and this observation is consistent with the above-mentioned results that furan-containing oligoaryls, in particular **28**, are efficient hole-transporting materials in an electroluminescent sandwich device.

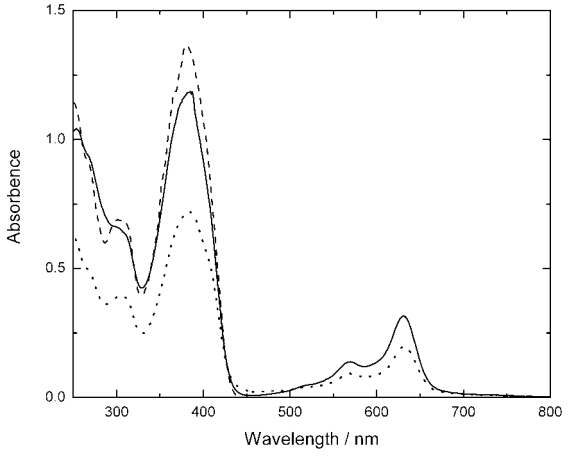
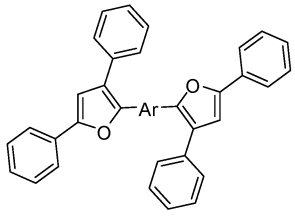


Fig. 1 Absorption spectra of **28** and its radical cations **30**. Dashed line: the absorption spectrum of **28**; solid line: radical cation **30** generated by applying a potential of 582 mV; dotted line: radical cation **30** generated by treatment of **28** in CH_2Cl_2 with few drops of concentrated H_2SO_4.

The furan moieties in alternating benzene-furan oligoaryls can be selectively oxidized by electrochemical methods. Thus, potentiostatic bulk electrolyses of **28** at 700 mV gives selectively diketone **31** in 90 % yield [25]. On the other hand, when a 1100 mV potential is applied, tetraketone **32** is isolated in 92 % yield.



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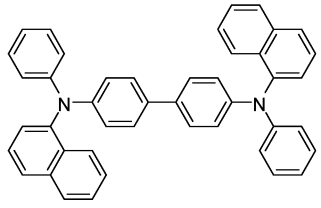

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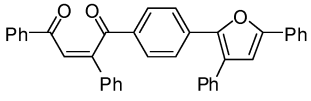

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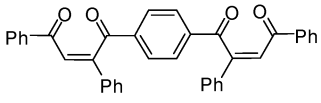

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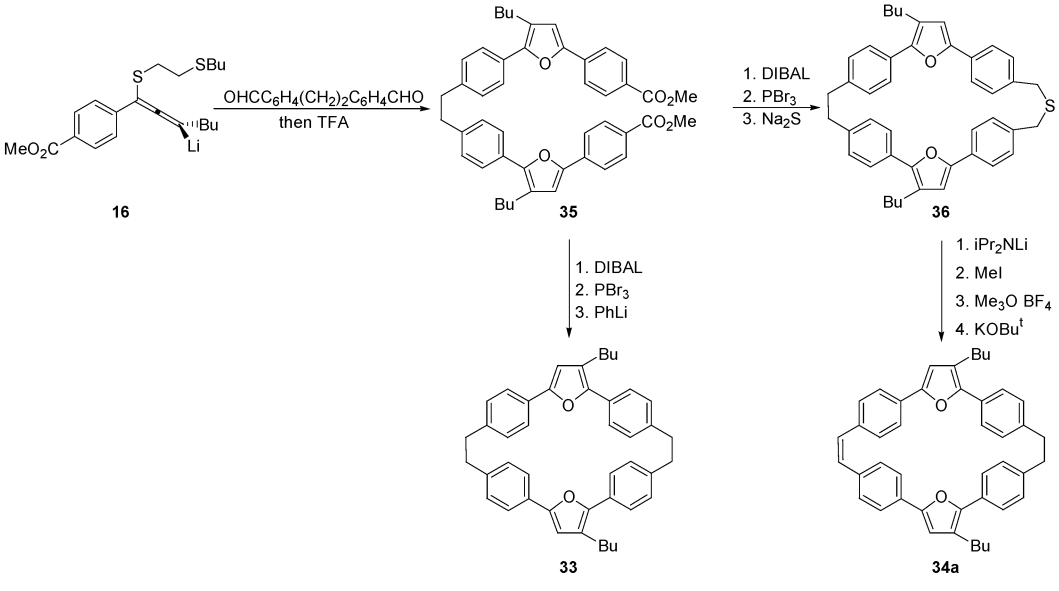
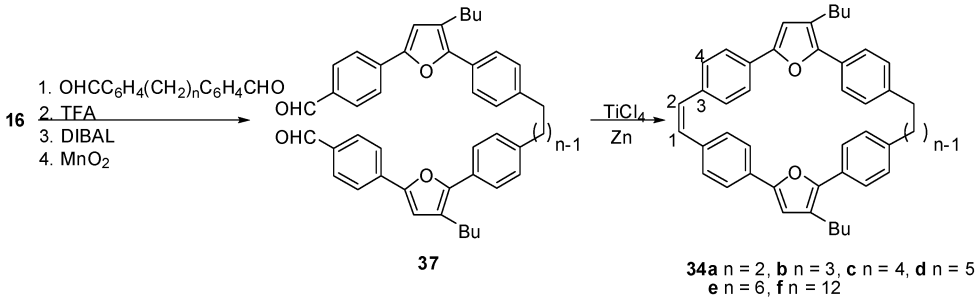
SYNTHESIS OF FURAN-CONTAINING [n.2]CYCLOPHENES

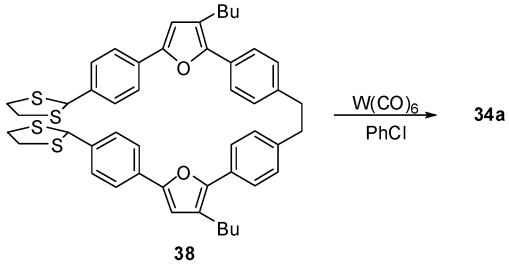
Cyclophanes have provided useful models for the investigation of through space interaction between chromophores [26,27]. In general, the conjugation length and the orientation of the chromophores may play a distinctive role in this respect. Moreover, incorporation of a double bond in the tethering aliphatic chain(s) such as cyclophenes and cyclophandienes may alter the geometry of the molecules which may lead to unusual photophysical properties [28–30]. In the previous sections, we have demonstrated the unique synthetic approaches and useful physical properties of alternating benzene-furan oligomers. By using a similar protocol, furan-containing teraryl cyclophane **33** and cyclophene **34a** are synthesized (Scheme 5) [31]. The bridging double bond in **34** can also be generated by McMurry coupling reaction (Scheme 6), and this route has been used for the synthesis of [n.2]cyclophenes **34** [32]. Alternatively, desulfurdimerization reaction of bis-dithioacetal **38** has been employed for the synthesis of **34a** (Scheme 7) [33]. Both **33** and **34a** are highly fluxional, and the barriers are estimated to be less than 9 kcal mol^{-1} [31].



Scheme 5



Scheme 6

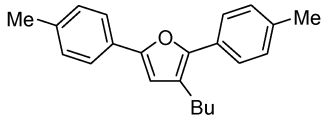


Scheme 7

Cyclophane **33** exhibits reversible two-electron redox process electrochemically, and the two oligoaryl moieties in **33** are oxidized independently at 0.614 V with reference to ferrocene/ferrocenium ion. This observation indicates that there would be little interaction between the two teraryl moieties in **33**. On the other hand, the presence of the double bond might contribute to the conjugative interactions between the two oligoaryl moieties in **34a**, and two sequential oxidation potentials at 0.540 and 0.665 V are observed [31].

PHOTOPHYSICS OF [n.2]CYCLOPHENES

The absorption and fluorescence profiles of **33**, **34a** are compared with those of the dimethylteraryl **39** (Fig. 2). In general, linear alternating benzene-furan oligoaryls exhibit very strong emission with high quantum yield [18–20,22,23]. Interestingly, both absorption and emission spectra of **33** have similar profiles at similar wavelengths as those of the unbridged teraryl **39** (λ_{em} ca. 380 nm). However, the quantum yield of **33** (0.59) is somewhat lower than that of **39** (0.83) [31]. The observation of similar vibronic structures in **33** and **39** again suggests that there is little interaction between two teraryl moieties in **33**.



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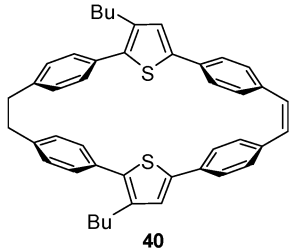

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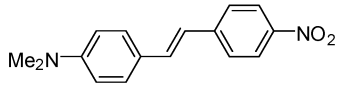

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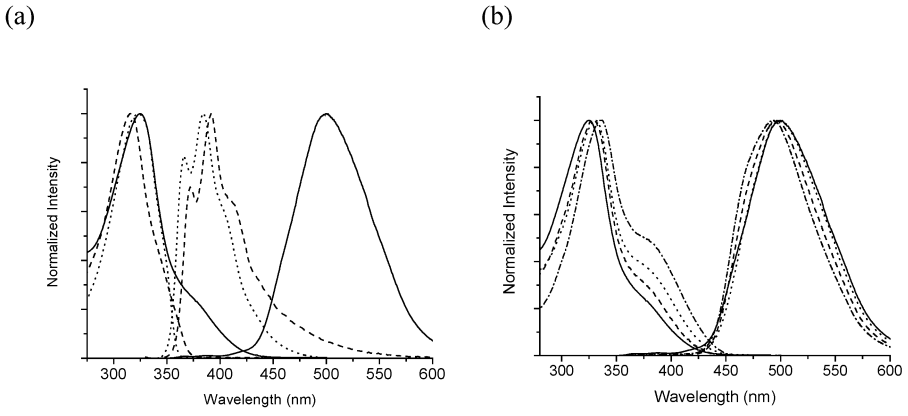

Fig. 2 (a) Absorption and emission spectra of **33** (dashed line), **34a** (solid line), and **39** (dotted line) in $CHCl_3$. (b) Absorption and emission spectra of **34a** (solid line), **34c** (dashed line), **34e** (dotted line), and **34f** (dashed–dotted line) in $CHCl_3$.

The photophysical properties of furan-containing [n.2]cyclophenes **34**, however, are extraordinary [31,32]. As shown in Fig. 2a, the absorption spectrum of **34a** exhibits a low energy band extended from ca. 350 nm in addition to the absorption due to the teraryl chromophore around 330 nm. The emission profile of **34a** is striking, large Stokes shift being observed. It seems likely that interactions between the teraryl portions and the double bond in **34a** may play an important role in thees interesting photophysical properties. Other cyclophenes behave similarly (Fig. 2b).

DFT/6-31G** calculations of **34a** show that the electron density distribution in the highest occupied molecular orbital (HOMO) is populated on two furan moieties, whereas electron density shifts to the bridging double bond in the lowest unoccupied molecular orbital (LUMO) (Fig. 4). Such electron distributions in HOMO and LUMO of **34a** may resemble donor and acceptor, respectively. Similar behavior is also found in **34b–f** and thiophene derivative **40**. On the other hand, the electron distributions in both HOMO and LUMO for **33** are superimposed and no charge transfer would occur (Fig. 3).

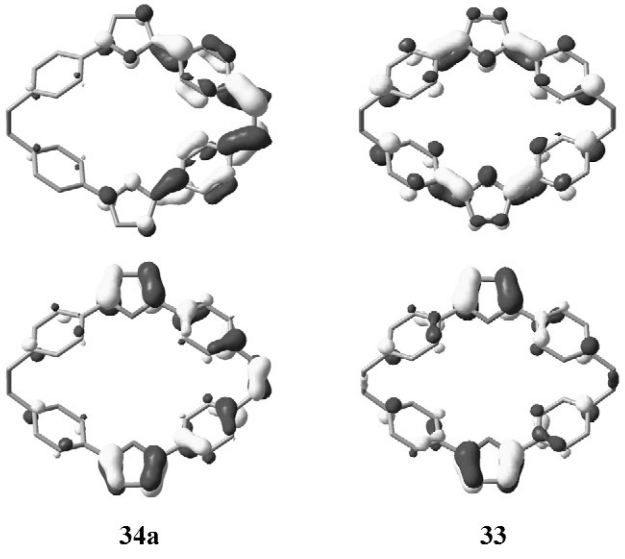

Fig. 3 Electron density distributions of HOMO and LUMO of **34a** and **33**.

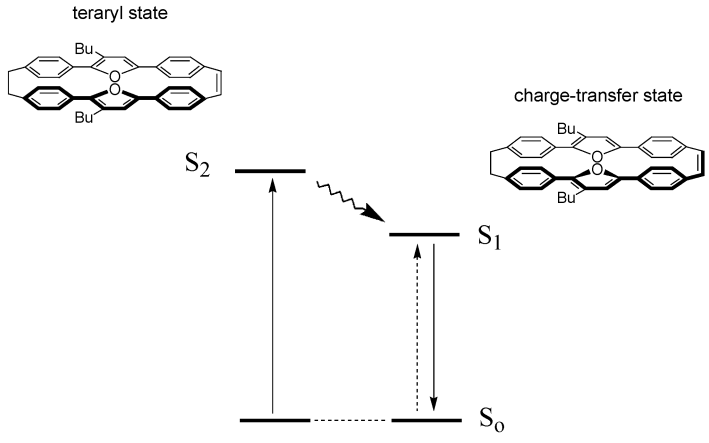

Fig. 4 Energy diagram of **34a** [26].

The photophysical properties of **34a** can be rationalized by perturbation theory (Fig. 4). The absorption band around 330 nm for **34a** is only slightly bathochromically shifted than those for **33** and **39**. This absorption may be attributed to the excitation from the S_0 to S_2 state of **34a**, which is mainly contributed from the teraryl moiety. In comparison to the S_2 state, the low-lying S_1 state in **34a** may be considered mainly as a charge-transfer state. In this regard, the S_1 state for electronic excitation with charge-transfer character would have lower energy. As such, when the absorption transition takes place, the wavelength would be red-shifted, and longer wavelength tailing around 380 nm can thus be rationalized. Within this context, the emission from the S_1 state may lead to large Stokes shifts.

SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF [n.2]CYCLOPHENES

The presence of donor and acceptor moieties conjugated with the linking π-system is known to facilitate the formation of intramolecular charge transfer, which will induce second-order NLO property [34]. As mentioned in the previous section, interaction between the teraryl chromophores and the bridging double bond may take place leading to charge-transfer character. It is well known that 2-furyl or 2-thienyl moiety is an electron-rich species with σ^+ values –0.39 and –0.43, respectively [35]. In other words, these heterocycles may serve as an electron donor in **34**. In this regard, one might consider that the bridging alkene group might be an electron acceptor. Recently, it has been shown that twisted π-electron system chromophores in a biaryl system having charged donor and acceptor moieties exhibit ultralarge molecular hyperpolarizability with exceptionally high μβ values [36,37]. It is envisaged that **34** and related compounds may be second-order NLO active. The photophysical properties and the μβ values (obtained by the electric field-induced second harmonic generation, EFISH, measured in $CHCl_3$ at 1.91 μm) for these compounds are summarized in Table 1 [32].

As can be seen from Table 1, cyclophenes **34a–f** and **40** exhibit second-order optical nonlinearity. The μβ values for **34a–e** are two orders higher than that for **34f** and that of **34d** is fivefold larger than that of **34e**. It is interesting to note that the μβ values for **34b–d** are comparable with that for **41**. The dipole moment for **41** is 6.6 debye [38]. Cyclophenes **34** are much less polar, and the calculated dipole moments of **34** are also outlined in Table 1. Replacement of the furan ring by a thiophene ring in **40** has the μβ value 203×10^{-48} esu, which is similar to that of **34a**. The contribution of the double bond to the NLO properties in **34a–f** and **40** is striking. It is worth mentioning that the saturated cyclophane **33** does not exhibit any NLO behavior and was even less polar (μ = 0.27 D). These results strongly indicate that the bridging double bond may be viewed as an electron acceptor in these novel cyclophenes.

Table 1 Photophysical and μβ values of **34** and related compounds in $CHCl_3$.

	λ_{max} (nm)	λ_{em} (nm)	Φ[a]	μ (D)[b]	$\mu\beta_{1.91}$[c]
34a	325	501	0.28	1.12	232
34b	327	506	0.32	1.23	370
34c	330	496	0.36	1.26	530
34d	330	498	0.39	1.29	502
34e	331	498	0.51	1.48	110
34f	337	494	0.57	1.05	3
40	314	494	0.22	1.14	203
33	315	380	0.59	0.27	n.d.
41	430			6.60[d]	450

[a]Measured in EtOAc using coumarin 1 as reference.
[b]Calculated by DFT at 6-31G** level.
[c]In 10^{-48} esu.
[d]Ref. [38].

CONCLUSIONS

By adopting our furan annulation protocol, a series of monodispersed alternating benzene-furan molecular wires up to 15 nm can be conveniently obtained. In addition, we have synthesized a new series of furan-containing teraryl cyclophene derivatives **34** which exhibit unusually large Stokes shifts and NLO properties. These cyclophenes **34** have neither particularly strong electron-donating moieties nor electron-withdrawing groups and have relatively low polarity. Yet they exhibit exceptionally high μβ values, which are even comparable with that of highly polar **41**. Structurally, the strained cyclophenes **34** furnish a unique feature to dictate these unusual photophysical properties. Because of strain, the π-systems in teraryl system and in the bridged double bond are twisted. Such a twisted system may thus induce significant enhancement in hyperpolarizability [36,37]. The five-membered heteroaromatic rings in **34** may not only serve as electron donors, but also accommodate the appropriate geometry to enable the interactions between the oligoaryl systems and the double bond, leading to unusual photophysical and NLO properties.

ACKNOWLEDGMENTS

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