# Journal of Materials Chemistry C

Materials for optical and electronic devices

www.rsc.org/MaterialsC

Volume 1 | Number 25 | 7 July 2013 | Pages 3889-4044



ISSN 2050-7526

# RSCPublishing





# Journal of Materials Chemistry C

# PAPER

Cite this: J. Mater. Chem. C, 2013, 1, 3917

Received 3rd April 2013 Accepted 10th May 2013 DOI: 10.1039/c3tc30611a

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## Introduction

Stimuli responsive self-organized architectures with functional properties hold great promise in design and fabrication of smart soft materials. Cholesteric liquid crystals (CLCs) represent such a striking example due to their unique self-organized helical arrangement of mesogen molecules and their property of selective reflection of light.<sup>1-5</sup> Moreover, the weak intermolecular interaction in liquid crystals (LCs) provides the possibilities of being responsive to a number of stimuli, such as light, heat, electric field, and mechanical stress. Among all stimuli, light is particularly attractive due to the advantages such as easy addressability, fast response time and potential for remote control in a wide range of ambient environments. Photoresponsive CLCs can be made by doping chiral photochromic molecules into an achiral nematic LC (NLC) host. The resulting mixture can self-organize into controllable, optically tunable helical superstructures, *i.e.* the cholesteric mesophase, which can selectively reflect light according to Bragg's law. The central

# A photoswitchable and thermally stable axially chiral dithienylperfluorocyclopentene dopant with high helical twisting power<sup>†</sup>

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A chiral dithienylperfluorocyclopentene molecule bearing two bridged binaphthyl units was designed and synthesized by a Suzuki–Miyaura cross-coupling reaction between chiral binaphthyl iodide and dithienylperfluorocyclopentene-derived bis(boronic ester). Its photoresponsive properties were investigated in both organic solvent and liquid crystal media. The UV-vis spectra exhibited typical photochromic changes of diarylethenes upon UV irradiation. The CD spectral changes upon light irradiation indicated that the conformation of binaphthyl units and the chiroptical properties of this molecule could be modulated by light. More importantly, when using as a chiral dopant in nematic liquid crystals, this molecule could induce cholesteric liquid crystals with very high helical twisting powers. At very low doping concentrations, this dopant was able to induce a reversible isothermal phase transition between nematic and cholesteric phases upon light irradiation. The photochemical control of the pitch length of cholesteric phases at higher doping concentrations enabled the reversible reflection wavelength control in the visible region. Superior thermal stability and excellent fatigue resistance were also observed during the photoswitching process, which are important properties for applications.

wavelength  $\lambda$  of the selective reflection is defined by  $\lambda = nP$ , where *P* is the pitch length of the helical structure across which the LC directors rotate a full  $360^{\circ}$  and *n* is the average refractive index of the LC material. The ability of a chiral molecule to induce a twist in the director orientation of an achiral NLC is quantified as the helical twisting power (HTP,  $\beta_{\rm M}$ ) and expressed in the equation  $\beta_{\rm M} = (PC)^{-1}$ , where C is the molar concentration of the chiral dopant. The reversible photoisomerization of a chiral dopant often results in a change in the HTP and therefore the reflection wavelength of the cholesteric phase can be reversibly tuned by light (Fig. 1). This provides opportunities as well as challenges in fundamental science that may pave the way for applications of CLC materials in color filters and reflectors,6-8 tunable lasers,9,10 and reflection displays11,12 which require no driving electronics and can be flexible.

High HTPs are of key importance for the performance of photoresponsive CLC materials since low HTPs give rise to the need for higher dopant concentrations for a specific pitch length. This often leads to phase separation, coloration and can alter the desired physical properties of the NLC host. To date, various kinds of photochromic molecules have been reported as chiral dopants for LCs, such as azobenzenes,<sup>13-19</sup> overcrowded alkenes,<sup>20–23</sup> diarylethenes,<sup>24–32</sup> spirooxazines<sup>33,34</sup> and fulgides.<sup>35,36</sup> Among them, diarylethenes are of particular interest owing to their thermal stability and fatigue resistance. Upon irradiation with UV light, they can transform from a colorless

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Measurement of pitch and HTP, thermal stability, fatigue resistance, CD spectra and copies of  $^1\rm H$  NMR and  $^{13}\rm C$  NMR. See DOI: 10.1039/c3tc30611a



**Fig. 1** Schematic illustration of the mechanism for the pitch length and reflection wavelength photo-tuning of the cholesteric phase using a chiral photo-chromic dopant.



**Scheme 1** Synthesis of intermediates and compound (*R*,*R*)-**1**. *Reaction conditions*: (a) CH<sub>2</sub>I<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, acetone; (b) (1) *t*-BuLi, THF, -78 °C, (2) I<sub>2</sub>; (c) Br<sub>2</sub>, CHCI<sub>3</sub>; (d) (1) *n*-BuLi, Et<sub>2</sub>O, (2) perfluorocyclopentene; (e) (1) *n*-BuLi, (2) B(OBu)<sub>3</sub>; (f) Pd(PPh<sub>3</sub>)<sub>4</sub>, aq. Na<sub>2</sub>CO<sub>3</sub>.

open-ring form to a colored closed-ring form. The closed form is thermally stable and the reverse photoisomerization to open form can occur only by visible light irradiation. The photochemically reversible switching of diarylethenes with thermal stability in both states constitutes the basis for their widespread applications in optical devices.<sup>37</sup> In comparison with the large body of literature describing the reflection color tuning of CLCs using chiral azobenzene molecules, the development of chiral diarylethene dopants with satisfactory functionalities for device performance, *e.g.* high HTPs, remains a challenging task.

The most frequently investigated diarylethenes are dithienylethenes with a cyclopentene or perfluorocyclopentene bridge. Although non-fluorinated dithienylcyclopentenes possess the advantage of low synthetic cost with acceptable performance, dithienvlperfluorocyclopentenes are more attractive due to their superior thermal stability and excellent fatigue resistance, which are crucial traits for switching and application purposes.38 In continuation of our research on diarylethenes,<sup>31,32</sup> here we report the synthesis and characterization of a new dithienvlperfluorocyclopentene (R,R)-1 containing two bridged binaphthyl units (Scheme 1). This compound was found not only to exhibit higher HTPs than previously reported diarylethene dopants but also to show excellent thermal stability and fatigue resistance. The intent behind the design of the molecular structure is derived from (1) axially chiral binaphthyl derivatives, particularly bridged ones are powerful CLC inducers with very high HTPs,39,40 (2) dithienylperfluorocyclopentene is selected as the core due to its excellent photochromic properties and fatigue resistance, and (3) the binaphthyl units can be directly attached to the photochromic core by the Suzuki-Miyaura protocol. These relatively more rigid structures are expected to increase HTPs of the resulting molecules.41

# **Results and discussion**

## Synthesis of compound (R,R)-1

Compound (R,R)-1 was synthesized by a Suzuki–Miyaura crosscoupling reaction between binaphthyl-derived iodide (R)-3 and bis(boronic ester) 7 (Scheme 1).<sup>42</sup> The intermediate (R)-3 was readily prepared in two steps starting from (R)-binol. The etherification of (R)-binol with diiodomethane gave the bridged product (R)-2, which underwent direct orthometalation in the presence of tert-butyllithium followed by quenching with iodine. By controlling the ratio of *tert*-butyllithium to (R)-2, mono-iodide (R)-3 was achieved in acceptable yield with a small portion of 3,3'-diiodide byproduct. Another key intermediate dichloride 6 was prepared according to a known method43 from 2-chloro-5-methyl thiophene 4, which was brominated to provide 3-bromo-5-chloro-2-methyl thiophene 5. Treatment of 5 with *n*-butyllithium and the following double substitution reaction with perfluorocyclopentene gave dichloride 6 in a moderate yield, which was converted to bis(boronic ester) 7 followed by the Suzuki-Miyaura cross-coupling reaction with iodide (R)-3 to afford the product (R,R)-1 in good yield. All the target compound and intermediates were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS or elemental analysis.

#### Photoisomerization in organic solvent

Compound (R,R)-1 is chemically and thermally stable, and its photoresponsive properties in solution were examined by UVvis spectroscopy (Fig. 2). The solution of (R,R)-1 in hexane was colorless and the UV spectrum showed maximum absorption at 279 nm, and there was no absorption observed in the visible region. Upon UV irradiation at 310 nm, the solution color changed immediately from colorless to fresh blue. Accordingly, there was a gradual decrease seen in the absorption at 279 nm accompanied by the appearance of a new absorption band in the visible region with a maximum at 612 nm (Fig. 2A), indicating the transformation of (R,R)-1 from its open form to the closed form. An isosbestic point remained at 331 nm during this process. The photostationary state (PSS<sub>310nm</sub>) was reached within 45 s and this irradiated state was thermally stable and could be switched back to the initial state upon visible light irradiation at 630 nm in about 10 minutes as evidenced by the restoration of the absorption spectra (Fig. 2B). The thermal stability of the closed form of (R,R)-1 at PSS<sub>310nm</sub> was monitored by the absorbance at 612 nm (A) compared with the initial absorbance  $(A_0)$  of PSS<sub>310nm</sub>. The plot of  $\ln(A/A_0)$  versus time shows the first order kinetics of the thermal decay and the halflife time is calculated to be 115 days (Fig. S1 and S2<sup>†</sup>). Furthermore, the photoisomerization in organic solvent also exhibited excellent fatigue resistance as revealed by the repeated irradiation of the sample with UV and visible light over many cycles (Fig. S3<sup>†</sup>).

The chiroptical property of (R,R)-1 in organic solvent was investigated by CD spectra at room temperature.  $\Delta \varepsilon$  is defined as the difference value between the molar excitation coefficients of left ( $\varepsilon_{\rm L}$ ) and right ( $\varepsilon_{\rm R}$ ) circularly polarized light, respectively. As shown in Fig. 3, the CD spectra of (R,R)-1 in hexane exhibited two



**Fig. 2** Absorption spectral changes of (*R*,*R*)-**1** (10  $\mu$ M in hexane) upon UV irradiation at 310 nm for different times (A) and the reverse process upon visible light irradiation at 630 nm (B). Inset: color change before and after UV irradiation.



**Fig. 3** CD spectral changes of (*R*,*R*)-**1** (10  $\mu$ M in hexane) upon UV irradiation at 310 nm for different times. Note:  $\Delta \varepsilon$  was calculated based on the molar concentration of (*R*,*R*)-**1**. Taking into account that there are two binaphthyl units, the conformation change of binaphthyl was estimated from the value of  $\Delta \varepsilon/2$ .

strong bisignated exciton couplets between 200 and 250 nm in the initial state, which are assigned to the coupling of the two  ${}^{1}B_{b}$ transitions located on distinct naphthalene rings.<sup>44</sup> The intense negative exciton couplet at 229 nm associated with a positive couplet at 216 nm reflect the absolute *R* configuration of the binaphthyl moiety in the molecule. The couplets at around 280 and 320 nm are related to the  ${}^{1}L_{a}$  and  ${}^{1}L_{b}$  transitions of naphthalene. Dramatic changes in shape and intensity were found in CD spectra when irradiated the solution with UV light at 310 nm. The exciton couplet at 229 nm weakened significantly with a small bathochromic shift in maximum to 231 nm. For the  ${}^{1}L_{a}$ and  ${}^{1}L_{b}$  transitions, the intensity of the positive band at around 280 nm decreased with a negative shoulder developing at 264 nm, while the negative band at 320 nm became nearly flat.

Binaphthyl derivatives can rotate along the carbon-carbon bond between the 1 and 1' positions in a certain range. The intensity change of <sup>1</sup>B<sub>b</sub> transitions is actually a sign of the conformation change in the binaphthyl moiety with variation in the dihedral angle  $(\theta)$  between two naphthalene rings.<sup>45</sup> Although the binaphthyls in (R,R)-1 are fixed with a methylenedioxy tether and thus have less flexibility, a slight variation of the dihedral angle is still possible, which may cause a dramatic difference in chiroptical properties.<sup>39,40,44</sup> According to Rosini's correlation between the  $\Delta \varepsilon$  of the low energy component of <sup>1</sup>B<sub>b</sub> exciton couplet (around 230 nm) and the dihedral angle of binaphthyl derivatives,<sup>45</sup> the  $\theta$  for the open form isomers was estimated to be around 60°, which is consistent with the fact that methylenedioxy bridged binaphthyl has a rigid structure with a quite narrow dihedral angle.46,47 The decrease in  $\Delta \varepsilon$  indicates that the dihedral angle in (R,R)-1 may be slightly increased during photoisomerization.<sup>45</sup> It is noteworthy that the photocyclization of (R,R)-1 generates two new chiral centers with the configuration of (S,S) or (R,R), and thus forms two diastereomers in closed form (Fig. S4<sup>†</sup>). However, no Cotton effect in the CD spectra was observed in the visible region around 612 nm corresponding to the absorption band of the closed form (Fig. S5<sup>†</sup>), indicating that no diastereoselective photoisomerization occurred in this photoisomerization process. Therefore the chiroptical properties of (R,R)-1 and their changes upon UV irradiation are mainly attributed to the binaphthyl units and the variation in dihedral angle.30

#### Photoisomerization in LC media

It is established that the dihedral angle in the binaphthyl derivative plays a key role in their cholesteric induction behaviors, such as HTP and handedness of the induced cholesteric phase.<sup>46,47</sup> Both the *transoid* conformation ( $\theta > 90^{\circ}$ ) and the *cisoid* conformation ( $\theta < 90^{\circ}$ ) of binaphthyl derivatives can efficiently induce CLCs with high HTPs, while the *quasi-orthogonal* conformations ( $\theta \sim 90^{\circ}$ ) only have very weak induction ability. For *R* configuration, the *transoid* conformation results in a left-handed CLC and the *cisoid* conformation results in a left-handed CLC. A change in  $\theta$  can cause a dramatic difference in the cholesteric induction abilities, *i.e.*, HTPs. Inspired by the chiroptical property information obtained from CD spectra, the photoresponsive behaviors of (*R*,*R*)-**1** in liquid crystals were then investigated.

NLC 4-pentyl-4'-cyanobiphenyl (5CB) was used as the host material. A cholesteric phase was observed under the polarized microscope with the characteristic fingerprint texture at a low doping concentration of 0.26 mol% (Fig. 4A), indicating that (R,R)-1 exhibited very high HTP at the initial state. The pitch length of the cholesteric helix was measured by Cano's method.<sup>48</sup> When the mixture was filled into a wedge cell, the photoinduced pitch change was directly evidenced by shortening the distance between the Cano's lines upon UV irradiation (Fig. 4B and C). According to the relationship between HTP and pitch, it was concluded that the HTP of (R,R)-1 was increased during photoisomerization.

By doping different concentrations of (*R*,*R*)-1, the inverse of the pitch (1/P) proportionally increases with increase in the doping concentration and the absolute values of HTP are then determined as the slopes by plotting 1/P against dopant concentrations (Fig. S7<sup> $\dagger$ </sup>). The HTPs of (*R*,*R*)-1 in different NLCs at both states were measured and the results are summarized in Table 1. The handedness of these CLCs was determined by the contact method.49 As seen in Table 1, (R,R)-1 induced lefthanded CLCs in all three hosts due to the cisoid form of the binaphthyl moiety, and the high HTPs at both the initial state and  $PSS_{310nm}$  are ascribed to the narrow dihedral angle of (R,R)-1.<sup>39</sup> In addition to the high HTPs, the photoisomerization led to a dramatic increase in HTPs, which might be the result of the dihedral angle change of the binaphthyl units in this molecule.46,47 Using different LC hosts resulted in different intermolecular associations between the dopant and the host as evidenced by the variation in HTP values and changes in magnitude upon UV irradiation. It was found that NLC 5CB not only gave the highest HTPs but also showed the largest HTP

Table 1 HTPs of (R,R)-1 at different states in NLC hosts

NLC <sup>a</sup>	HTP $(\beta_{M})$			h
	Initial state	PSS <sub>310nm</sub>	PSS <sub>630nm</sub>	HTP change <sup>b</sup> $(\Delta \beta_{\rm M} / \beta_{\rm M})$
F7	_114	_145	_116	+27%
5CB	-147	-188	-110 -150	+28%
Zli-1132	-124	-141	-118	+14%

 $^a$  E7 is a eutectic mixture of LC components commercially designed for display applications, and 5CB is 4'-pentyl-4-biphenylcarbonitrile. Zli-1132 is a mixture of 4-(4-alkylcyclohexyl)benzonitrile and 4-(4-alkylcyclohexyl)-4'-cyanobiphenyl derivatives.  $^b$  Percent change in  $\beta_{\rm M}$  observed between the initial state and PSS<sub>UV</sub>.

change upon UV irradiation. The HTP of (*R*,*R*)-1 at the initial state in 5CB was 147  $\mu$ m<sup>-1</sup> while the highest HTP of the known chiral diarylethenes recently reported is 109  $\mu$ m<sup>-1</sup> at the initial state in 5CB,<sup>31</sup> which was further increased to 188  $\mu$ m<sup>-1</sup>. To the best of our knowledge, this is the highest value among the known diarylethene dopants so far.<sup>24-32</sup>

#### Light-induced isothermal phase transition

The light-induced isothermal phase transition between nematic and cholesteric is interesting and has been demonstrated with a few chiral dopants utilizing their large variations in HTPs between two different states. Compound (R,R)-1 was found to be able to induce the cholesteric mesophase even with the concentration as low as 0.13 mol% due to its high HTP at the initial state. When the doping concentration was further reduced to 0.1 mol%, the LC mixture exhibited an apparent nematic phase which was confirmed by the conoscopic observation (Fig. 5A), *i.e.* the pitch was too long to be detected at this low doping concentration. Upon UV irradiation at 310 nm, a characteristic fingerprint texture of the cholesteric phase gradually appeared due to the increase of HTP and the consequent formation of a helical superstructure of the cholesteric phase (Fig. 5B and C). The cholesteric phase at this irradiated state was thermally stable and the reverse process to the nematic phase occurred with visible light irradiation at 630 nm. All the experiments were carried out at room temperature and heating from light irradiation was not detected and thought to be minimal at the exposure intensity of 30 mW cm<sup>-2</sup>.



**Fig. 4** Cross-polarized optical texture of 0.26 mol% of (R,R)-**1** in 5CB (A) and the pitch change before (B) and after (C) UV irradiation observed in a wedge cell.



**Fig. 5** Cross-polarized optical textures of 0.1 mol% of (*R*,*R*)-**1** in 5CB in a 5  $\mu$ m thick homeotropic cell upon UV irradiation for 0 s (A, conoscopic observation), 5 s (B) and 30 s (C).

#### **Reflection color control**

Compound (R,R)-1 showed very good solubility in all the three NLC hosts. For the reflection wavelength tuning, we used 5CB as the NLC host due to the higher HTPs and larger HTP variation. At first, a LC mixture was formulated by doping 1.38 mol% of (R,R)-1 into 5CB, which was capillary-filled into a 5  $\mu$ m thick glass cell with anti-parallel rubbing directions. The cell was painted black on one side and the reflection spectra were recorded. At the initial state, the cell showed a reflection band in the near IR region with a central wavelength of ca. 800 nm, and no reflection color was observed visually (Fig. 6). After UV irradiation for 60 s to reach the photostationary state, the reflection band shifted to the visible region with a central wavelength of ca. 640 nm, and a red reflection color was visually observed in the cell. This pronounced hypochromic shift in reflection wavelength was a result of shortening in pitch, which was also in accordance with the increase in HTPs of (R,R)-1 during photoisomerization.

A higher doping concentration of 1.80 mol% enabled the phototuning of reflection wavelength in the visible region as demonstrated in Fig. 7. The reflection color of the cell at the initial state was orange-red with a central reflection wavelength of *ca.* 600 nm. Upon UV irradiation for 15 s, the reflection



**Fig. 6** Real cell images and reflection spectra of  $1.38 \mod 6$  of (*R*,*R*)-**1** in 5CB before (black) and after UV irradiation for 60 s (red).



**Fig. 7** Real cell images and reflection spectra of 1.80 mol% of (R,R)-**1** in 5CB upon UV irradiation at 310 nm for 0 s (orange), 15 s (green) and 60 s (blue).

wavelength was shifted to *ca*.550 nm and the cell showed a green reflection color, which was further tuned to blue with a reflection wavelength of *ca*. 470 nm at  $PSS_{310nm}$ . The reverse process was achieved with 630 nm visible light irradiation and it took about 10 minutes for the LC mixture to restore to the initial state (Fig. S8†). It is worth noting here that the LC mixture exhibited superior thermal stability in any irradiated state which was revealed by no obvious reflection wavelength shifting being detected when the cell was stored in the dark (Fig. S9†). The excellent fatigue resistance was examined by the repeated switching between the initial state and  $PSS_{310nm}$  over many cycles with no degradation in cell properties detected (Fig. S10†). Combined with the superior thermal stability and excellent fatigue resistance, the reflection color tuning enabled by (*R*,*R*)-1 is extremely promising for future applications.

## Conclusion

A new axially chiral dithienylperfluorocyclopentene dopant containing two bridged binaphthyl units was designed and synthesized. Its photoresponsive properties were investigated in both organic solvent and LC media. The photochromic behaviors in organic solvent were characterized by UV-vis and CD spectra. When used as a chiral dopant, it was found that this molecule exhibited very high HTPs in different NLC hosts. The light-induced isothermal phase transition between nematic and cholesteric was achieved with this dopant at a very low doping concentration. The reflection wavelength of the CLCs with higher doping concentrations was reversibly tuned in the visible region. Moreover, the photochemical switching also showed superior thermal stability at both states and excellent fatigue resistance. The high HTPs combined with excellent thermal stability and fatigue resistance are believed to be helpful for the development of more powerful molecular switches and represent progress towards practical applications.

## **Experimental section**

#### Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. Tetrakis-(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) and (R)-1,1'-bi(2naphthol) were purchased from Sigma-Aldrich. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or THF-d<sub>8</sub>. <sup>1</sup>H (400 MHz) and <sup>19</sup>F (376 MHz) NMR spectra were recorded on a Bruker 400 spectrometer and <sup>13</sup>C (50 MHz) was recorded on a Varian 200 spectrometer. Chemical shifts are in  $\delta$  units (ppm) with the residual solvent peak or TMS as the internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh  $F_{254}$  glass plates. Spots were rendered visible by exposing the plate to UV light. Melting points are uncorrected. Elemental analysis was performed by Robertson Microlit Inc. The mass spectrum was taken by Mass Spectrometry & Proteomics Facility

of Ohio State University. Textures and disclination line distance changes were observed by optical microscopy using a Leitz or Nikon polarizing microscope. UV-vis spectra were measured by a Perkin Elmer Lambda 25 Spectrometer. Circular dichroism (CD) spectra were recorded on a J-715 spectropolarimeter (Jasco Inc.). The UV and visible light irradiation was carried out using a xenon light source 100 W through a filter at 310 nm or 630 nm. Reflection spectra were examined with an Ocean Optics spectrometer collecting spectra in the dark. The achiral NLCs E7, 5CB and Zli-1132 were used in the study. E7 is a eutectic mixture of LC components commercially designed for display applications and 5CB is 4'-pentyl-4-biphenylcarbonitrile. Zli-1132 is a mixture of 4-(4-alkylcyclohexyl)benzonitrile and 4-(4-alkylcyclohexyl)-4'-cyanobiphenyl derivatives.

#### Measurement of pitch and HTP

The CLCs were prepared by weighing appropriate amounts of host liquid crystal and the dopant into a vial followed by mixing them with the addition of a few drops of dichloromethane. After evaporation of the solvent under reduced pressure, the mixture was loaded into the wedge cell by capillary action at room temperature. The pitch was then determined by measuring the intervals of Cano's lines appearing on the surfaces of wedge type liquid crystalline cells. Three different concentrations were used by this method for each sample, and the HTP was determined by plotting  $1/P (\mu m^{-1})$  against the concentration of the dopant *C* (mol%) according to the equation  $\beta_{\rm M} = 1/(PC)$ .

#### (R)-2,2'-Methylenedioxy-1,1'-binaphthyl (R)-2 (ref. 31)

A mixture of (*R*)-1,1'-bi(2-naphthol) (1.43 g, 5 mmol), diiodomethane (4.01 g, 15 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (4.14 g, 30 mmol) in acetone (50 mL) was stirred magnetically and refluxed until the reaction was complete as monitored by TLC. After cooling to room temperature, the reaction mixture was poured into water and extracted with ether (3 × 50 mL). The combined organic layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude product was purified by flash column chromatography over silica gel to give the product as a white solid (1.37 g, 92%). Mp: 186–188 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  = 8.01–7.92 (m, 4H), 7.54–7.41 (m, 6H), 7.35–7.30 (m, 2H), 5.70 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz)  $\delta$  = 151.2, 132.2, 131.8, 130.3, 128.4, 126.9, 126.08, 126.05, 125.0, 120.9, 103.1. HRMS (ESI) calcd for C<sub>21</sub>H<sub>14</sub>O<sub>2</sub>Na<sup>+</sup>: 321.0891, found: 321.0898.

#### (R)-3-Iodo-2,2'-methylenedioxy-1,1'-binaphthyl (R)-3 (ref. 31)

To a THF solution (40 mL) of (*R*)-2 (596 mg, 2 mmol) at -78 °C under nitrogen was added *t*-BuLi (1.5 mL, 1.7 M in pentane, 2.5 mmol). The solution was stirred at this temperature for 1 h. To the resulting solution was added a solution of I<sub>2</sub> (660 mg, 2.6 mmol) in THF (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for an additional 10 h. The excess iodine was reduced with 1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The reaction mixture was poured into water, and extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography to give the product as a white solid

(382 mg, 45%). Mp: 208–210 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 8.50 (s, 1H), 8.00 (d, J = 9.2 Hz, 1H), 7.94 (dd, J = 8.8, 1.2 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.50–7.43 (m, 5H), 7.33–7.28 (m, 2H), 5.71 (d, J = 3.6 Hz, 1H), 5.67 (d, J = 3.6 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz)  $\delta$  = 151.5, 149.3, 139.2, 133.1, 132.0, 131.7, 130.7, 128.4, 127.3, 127.0, 126.9, 126.7, 126.5, 126.2, 125.8, 125.1, 120.8, 102.6, 90.2. Anal. calcd for C<sub>21</sub>H<sub>13</sub>IO<sub>2</sub>: C, 59.45, H, 3.09; found: C, 59.22, H, 2.94%. HRMS (ESI) calcd for C<sub>21</sub>H<sub>13</sub>IO<sub>2</sub>Na<sup>+</sup>: 446.9858, found: 446.9840.

#### 3-Bromo-5-chloro-2-methylthiophene (5) (ref. 43)

A solution of bromine (4.8 g, 30 mmol) in chloroform (10 mL) was added dropwise into an ice-cooled solution of 2-chloro-5methyl thiophene 4 (3.99 g, 30 mmol) in chloroform (50 mL). After addition of the bromine, the reaction mixture was stirred for 2 h at room temperature, and subsequently poured into water (100 mL). The mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with 1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by flash column chromatography to give the product as a yellow oil (5.5 g, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  = 6.73 (s, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz)  $\delta$  = 133.1, 128.4, 126.8, 107.5, 14.7. The NMR data are in accordance with the literature.

# 1,2-Bis(5-chloro-2-methyl-3-thienyl)perfluorocyclopentene (6) (ref. 43)

To a stirred solution of 3-bromo-5-chloro-2methylthiophene (3.0 g, 14.2 mmol) in anhydrous diethyl ether (50 mL), n-butyllithium (9.75 mL, 1.6 M in hexane, 15.6 mmol) was added dropwise at -78 °C and the resulting solution was stirred for 15 min. Pre-cooled perfluorocyclopentene (1.38 g, 6.5 mmol) was added immediately and the mixture was kept at this temperature and stirred for another 4 h. Then the mixture was diluted with diethyl ether (50 mL) and the reaction was quenched with an aqueous solution of hydrochloric acid. The aqueous layer was extracted with diethyl ether (3  $\times$  50 mL) and the combined organic layers were washed with an aqueous solution of NaHCO<sub>3</sub> (50 mL), water (2  $\times$  50 mL) and brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by flash column chromatography to give the product as an off-white solid (1.08 g, 38%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta = 6.89$  (s, 2H), 1.89 (s, 6H). The NMR data are in accordance with the literature. Anal. calcd for C<sub>15</sub>H<sub>8</sub>Cl<sub>2</sub>F<sub>6</sub>S<sub>2</sub>: C, 41.20, H, 1.84; found: C, 41.35, H, 1.73%.

### (*R*,*R*)-1,2-Bis[2-methyl-5-(2,2'-methylenedioxy-1,1'-binaphthyl-3-yl)-3-thienyl]perfluorocyclopentene ((*R*,*R*)-1)

To a solution of **6** (218 mg, 0.5 mmol) in anhydrous THF (10 mL) was added *n*-BuLi (0.65 mL, 1.6 M in hexane, 1 mmol) dropwise, and the mixture was stirred at room temperature for 1 h. Then B(OBu)<sub>3</sub> (345 mg, 1.5 mmol) was added and stirred at room temperature for another 1 h followed by addition of (*R*)-3 (425 mg, 1 mmol), 20% Na<sub>2</sub>CO<sub>3</sub> (8 mL) aqueous solution and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol). The reaction mixture was heated and stirred for 10 h. After the mixture was cooled to room

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temperature, the organic layer was separated and the water layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude product was purified by flash column chromatography over silica gel to give (*R*,*R*)-1 as an off-white solid (202 mg, 42%). Mp: 250–252 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  = 8.23 (s, 2H), 7.99 (d, 8.8 Hz, 2H), 7.96–7.92 (m, 4H), 7.67 (s, 2H), 7.51–7.42 (m, 10H), 7.34–7.28 (m, 4H), 5.67 (d, *J* = 3.6 Hz, 2H), 5.61 (d, *J* = 3.2 Hz, 2H), 2.09 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 151.2, 147.3, 142.6, 136.7, 132.1, 131.8, 131.6, 131.5, 130.6, 128.4, 127.6, 127.4, 126.8, 126.3, 126.2, 126.0, 125.9, 125.8, 125.6, 125.4, 125.1, 120.7, 102.4, 14.4. <sup>19</sup>F NMR (THF-d<sub>8</sub>, 376 MHz)  $\delta$  = -112.7 (t, *J* = 4.9 Hz, 4F), -134.7 to -134.8 (m, 2F). Anal. calcd for C<sub>57</sub>H<sub>34</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C, 71.24, H, 3.57; found: C, 71.47, H, 3.32%. MS (ESI): *m/z* 983 (M + Na<sup>+</sup>).

# Acknowledgements

This work is supported by the Air Force Office of Scientific Research (AFOSR FA9550-09-1-0254 and FA9550-09-1-0193).

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