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π-Conjugated Twin Molecules Based on Truxene: Synthesis and Optical Properties

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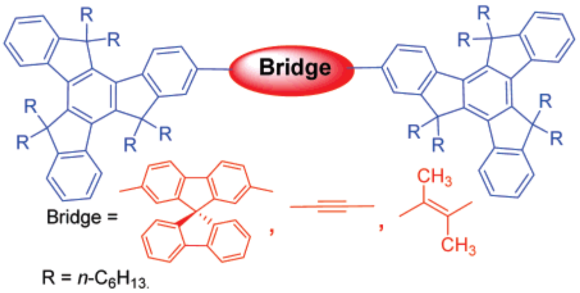
ABSTRACT



A series of novel extended π-conjugated twin molecules based on 10,15-dihydro-*5H*-diindeno[1,2-α;1′,2′-*c*]fluorene (truxene) have been prepared via Pd(0)-catalyzed Suzuki coupling, Sonogashira coupling, and McMurry reactions, respectively. 9,9′-Spirobifluorenylene, ethynylene, and vinylene groups as the bridge are introduced to connect both truxene moieties to understand the effect of the large steric chromophores on the properties of the desired materials. The investigation of optical properties of TM1–3 by UV–vis and photoluminescent spectroscopy demonstrates that the optical properties of the twin molecules are strongly affected by the π-linkages.

In modern electronics and optoelectronics, a myriad of opportunities for both academic and industrial scientists have been offered by organic and polymeric light-emitting diodes (OLEDs).[1] The flexibility of introducing diverse functionalities into molecules offers a much broader range of optical and electrical properties than for traditional semiconductors. In comparison with π-conjugated polymers (CPs), monodisperse conjugated oligomers possessing well-defined conjugation lengths and structural models are characterized by the uniformity, absence of chain defects, and ease of purification and characterization, which make them superior to CPs for systematic investigation of the structure−property relationships.[2]

Molecular structures have significant impact on the properties of organic materials. For instance, one crucial issue for the application of π-conjugated oligomers in organic optoelectronic devices is their ability to form morphologically stable and homogeneous films. To fulfill this requirement and others, several families of molecular architectures have been exploited, such as starburst molecules with C_3 sym-

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(1) (a) *Conjugated Polymers*; Brĕdas, J. L., Sylbey, R., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (b) *Conjugated Conducting Polymers*; Kies, H., Ed.; Springer: Berlin, 1992; Vol. 102. (c) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Ed.; Dekker: New York, 1997. (d) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. (e) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477. (f) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430. (g) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (h) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. *Adv. Mater.* **2000**, *12*, 1737. (i) Ho, P. K. H.; Kim, J. S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. *Nature* **2000**, *404*, 481. (j) Gross, M.; Müller, D. C.; Nothofer, H.-G.; Scherf, U.; Neher, D.; Bräuchle, C.; Meerholz, K. *Nature* **2000**, *405*, 661. (k) Miller, J. S. *Adv. Mater.* **1993**, *5*, 671. (l) Müller, D. C.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wlederhirm, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829.

(2) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, New York, 1998.

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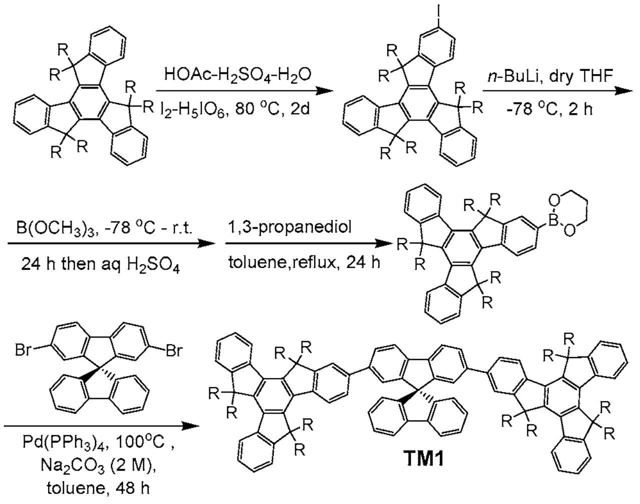
metry,[3] orthogonally fused spiro-type molecules,[4] paracyclophanes,[5] tetrahedral molecules,[6] dendrimers,[7] and twin molecules.[8] As the most straightforward approach, twin molecule couples two chromophore halves by either a flexible alkyl spacer or a rigid aromatic linkage. The electronic properties of the former are almost the same as those of the monomer, while the latter allows an extension of π-electronic conjugation, which increases the effective conjugation length of the whole molecule.

During the past decades, truxene has been recognized as the starting material for the construction of larger polyarenes and bowl-shaped fragment of the fullerenes, liquid crystals, C_3 tripod materials in asymmetric catalysis, and chiral recognition.[9] We prepared a series of star-shaped oligothiophenes-functionalized truxene derivatives and novel π-conjugated dendrimers based on truxene, which exhibited unique NMR behaviors, optical properties, and electroluminescence.[10] Herein, we report the initial synthesis of a series of π-conjugated twin molecules based on truxene, the truxene halves of which are connected by a rigid 9,9-spirobifluorenylene or ethynylene or vinylene linkage. We also investigate optical properties of these molecules, which shed light on the structure−property relationship of these dimeric molecules.

The readily available starting material **1** was prepared in our previous contributions.[10] Six hexyl groups were attached to the C-5, C-10, and C-15 positions of the truxene moiety to increase solubility as well as to release intermolecular $\pi-\pi$ stacking. As shown in Scheme 1, with a controlled amount of iodine and periodic acid hydrate, selective electrophilic iodination at one branch of the truxene segment afforded the monosubstituted truxene iodide **2** in good yield (83%).[11] Under nitrogen atmosphere, addition of n-butyllithium at −78 °C followed by addition of $B(OCH_3)_3$, hydrolysis by 50%

Scheme 1



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(3) (a) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145. (b) Higuchi, A.; Inada, H.; Kobata, T.; Shirota, Y. *Adv. Mater.* **1991**, *3*, 549. (c) Thelakkat, M.; Schmidt, H.-W. *Adv. Mater.* **1998**, *10*, 219. (c) Bettenhausen, J.; Strohriegl, P. *Adv. Mater.* **1996**, *8*, 507. (d) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018. (e) Kinoshita, M.; Shirota, Y. *Chem. Lett.* **2001**, *2001*, 614. (f) Bettenhausen, J.; Grezcmiel, M.; Jandke, M.; Strohriegl, P. *Synth. Met.* **1997**, *91*, 223.

(4) (a) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C.-H.; Su, Y.-O.; Lee, G..-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576. (b) Katsis, D.; Geng, Y. H.; Ou, J.-J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332. (c) Geng, Y. H.; Katsis, D.; Culligan, S. W.; Ou, J.-J.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 463. (d) Wu, C.-C.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chen, Y.-M.; Chien, Y.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 3710. (e) Geng, Y. H.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542. (f) Wu, F.-I.; Reddy, D. S.; Shu, C.-F.; Liu, M. S.; Jen, A. K.-Y. *Chem. Mater.* **2003**, *15*, 269. (g) Salbeck, J.; Yu, N.; Bauer, J.; Weissörtel, F.; Bestgen, H. *Synth. Met.* **1997**, *91*, 209. (h) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924. (i) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 8104.

(5) (a) Zyss, J.; Ledoux, I.; Volkov, S.; Chernyak, V.; Mukamel, S.; Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 11956. (b) Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 5183. (c) Bartholomew, G. P.; Ledoux, I.; Mukamel, S.; Bazan, G. C. Zyss, J. *J. Am. Chem. Soc.* **2002**, *124*, 13480. (d) Bartholomew, G. P.; Bazan, G. C. *Acc. Chem. Res.* **2001**, *34*, 30.

(6) (a) Yang, C. Y.; Wang, S.; Robinson, M. R.; Bazan, G. C. Heeger, A. J. *Chem. Mater.* **2001**, *13*, 2342. (b) Summers, M. A.; Kemper, P. R.; Bushnell, J. E.; Robinson, M. R.; Bazan, G. C. Bowers, M. T.; Buratto, S. K. *J. Am. Chem. Soc.* **2003**, *125*, 5199. (c) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695.

(7) (a) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. (b) Morgenroth, F.; Reuther, E.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 631. (c) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402. (d) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (e) Gong, L.; Hu, Q.-S.; Pu, L. *J. Org. Chem.* **2001**, *66*, 2358. (f) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 643. (g) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bassler, H. *Adv. Mater.* **2001**, *13*, 258. (h) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079. (i) Higuchi, M.; Shiki, S.; Ariga, K.; Yamamoto, K. *J. Am. Chem. Soc.* **2001**, *123*, 4414. (j) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509. (k) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. *Org. Lett.* **2002**, *4*, 2067. (l) Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691. (m) Bo, Z.; Rabe, J. P.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2370. (n) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864.

(8) (a) Tang, T. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714. (c) Barbarella, G.; Favaretto, L.; Zambianchi, M.; Pudova, O.; Arbizzani, C.; Bongini, A.; Mastragostino, M. *Adv. Mater.* **1998**, *10*, 551.

(9) (a) Gómez-Lor, B.; de Frutos, Ó.; Echavarren, A. M. *Chem. Commun.* **1999**, 2431. (b) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325. (c) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.* **2000**, *122*, 2719. (d) Rabideau, P. W.; Abdourazak, A. H.; Marcinow, Z.; Sygula, R.; Sygula, A. *J. Am. Chem. Soc.* **1995**, *117*, 6410. (e) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323. (f) Boorum, M. M.; Vasil'ev, Y. V.; Drewello, T.; Scott, L. T. *Science* **2001**, *294*, 828. (g) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500. (h) Cherioux, F.; Guyard, L. *Adv. Funct. Mater.* **2001**, *11*, 305. (i) Dijkstra, H. P.; Kruithof, C. A.; Ronde, N.; van de Coevering, R.; Ramón, D. J.; Vogt, D.; van Klink, G. P. M.; van Koten, G. *J. Org. Chem.* **2003**, *68*, 675. (j) Lambert, C.; Nöll, G.; Schämlzlin, E.; Meerholz, K.; Bräuchle, C. *Chem. Eur. J.* **1998**, *4*, 2129. (k) Perova, T. S.; Vij, J. K. *Adv. Mater.* **1995**, *7*, 919. (l) Fontes, E.; Heiney, P. A.; Ohba, M.; Haseltine, J. N.; Smith, A. B. *Phys. Rev. A.* **1988**, *37*, 1329. (m) Destrade, C.; Malthete, J.; Tinh, N. H.; Gasparoux, H. *Phys. Lett.* **1980**, *78A*, 82. (n) Gómez-Lor, B.; de Frutos, Ó.; Ceballos, P. A.; Granier, T.; Echavarren, A. M. *Eur. J. Org. Chem.* **2001**, *11*, 2107. (o) de Frutos, Ó.; Granier, T.; Gómez-Lor, B.; Jiménez-Barbero, J.; Monge, M. Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Chem. Eur. J.* **2002**, *8*, 2879. (p) Ruiz, M.; Gómez-Lor, Santos, A.; Echavarren, A. M. *Eur. J. Org. Chem.* **2004**, 858. (q) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.

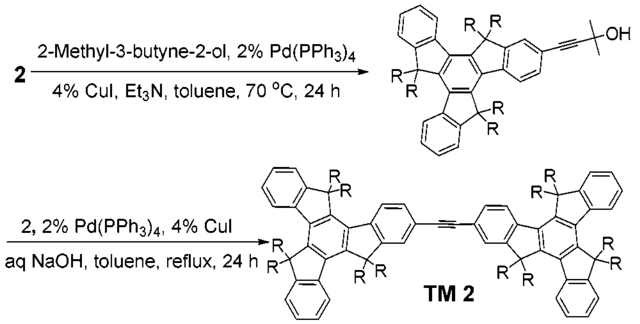
(10) (a) Pei, J.; Wang, J.-L.; Cao, X.-Y.; Zhou, X.-H.; Zhang, W.-B. *J. Am. Chem. Soc.* **2003**, *125*, 9944. (b) Cao, X.-Y.; Zhang, W.-B.; Wang, J.-L.; Zhou, X.-H.; Lu, H.; Pei, J. *J. Am. Chem. Soc.* **2003**, *125*, 12430. (c) Cao, X.-Y.; Liu, X.-H.; Zhou, X.-H.; Zhang, Y.; Jiang, Y.; Cao, Y.; Cui, Y.-X.; Pei, J. *J. Org. Chem.* **2004**, *69*, 6050.

(11) Lee, S. H.; Nakamura, T.; Tsutsui, T. *Org. Lett.* **2001**, *3*, 2005.

H_2SO_4 aqueous solution, and esterification by 1,3-propyldiol generated ester **3** in moderate yield (43%). The standard Suzuki coupling reaction[12] between **3** and 2,7-dibromo-9,9-spirobifluorene (**4**)[13] with $Pd(PPh_3)_4$ as catalyst in toluene provided the target molecule **TM1** efficiently (86%).

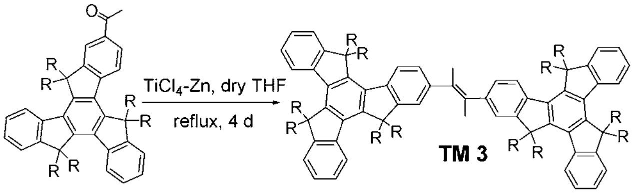
TM2 was prepared by repetitive palladium-catalyzed Sonogashira coupling reaction from **2** (Scheme 2). Acetylenic alcohol **5** was readily obtained via the Sonogashira coupling [$Pd(PPh_3)_4$, CuI, Et_3N] of iodide **2** and 2-methylbut-3-yn-2-ol.[14] It should be noted that the utilization of 2-methylbut-3-yn-2-ol instead of trimethylsilylacetylene (TMSA) is necessary to obtain pure intermediate, due to the increased polarity difference between the starting material and the product. The one-pot Sonogashira coupling between the acetylenic alcohol **5** and aryl iodide **2** took place in a two-phase heterogeneous system in the presence of a phase-transfer reagent and an aqueous base.[15] Under these conditions, acetylene alcohol **5** transformed into the arylethyne intermediate, which coupled with aryl iodide **2** immediately.

Scheme 2



TM3 was formed via a reductive coupling of two ketones **6**[10b] using the McMurry reaction[16] (Scheme 3). Prolonged reaction time and increased amounts of tetrachlorotitanium−zinc ($TiCl_4$−Zn) were crucial to get an excellent yield (93%).

Scheme 3



All new compounds have been characterized by a variety of spectroscopic techniques. The structures and purities of all target molecules (**TM1**−**3**) have been confirmed by ^1H and ^{13}C NMR spectra in $CDCl_3$, elemental analysis, as well as MALDI-TOF mass spectra (see the Supporting Information).

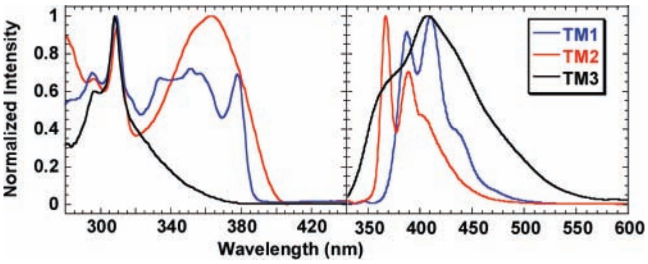


Figure 1. Normalized absorbance (left) and fluorescence (right) spectra of twin molecules **TM1**−**3** recorded in THF at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

The absorption and photoluminescent (PL) spectra of twin molecules were recorded in dilute THF solutions as shown in Figure 1. The photophysical properties were summarized in Table 1. Their solid films on quartz plates used for UV−vis and fluorescence characterization were spin coated with 2% toluene solution at 2000 rpm. All absorption spectra in dilute THF solutions exhibited a characteristic peak of the truxene chromophore (at about 309 nm). The λ_{max} for **TM1** was 362 nm, which red-shifted in comparison with the truxene moiety due to the increased conjugation length, while **TM2** exhibited two peaks at 352 and 380 nm, respectively. It's interesting that the absorption spectra of **TM3** was quite similar to that of truxene, indicating the poor conjugation between two truxene halves due to increased steric hindrance by two methyl groups. We observed that the absorption spectra of solutions and corresponding films are nearly identical. The absorption spectra in film states for all molecules did not show much hypsochromic shift (Figure 2), which implied that intermolecular $\pi-\pi$ aggregation was substantially suppressed in films owing to the large truxene moiety.

Table 1. Photophysical Properties of Twin Molecules **TM1**−**3**

twin molecules	λ_{max} abs (nm)		λ_{max} PL (nm)	
	solutions	films	solutions	films
TM1	**362**, 309	298, 311, **362**	388, **411**	394, **412**
TM2	295,**309**, 334, 351, 378	297, 303, **312**, 340, 352, 359, 380	**368**, 389	**392**, 409
TM3	297, **308**	298, **310**	408	431

The PL spectra of **TM1** in THF solution exhibited two characteristic peaks at 388 and 411 nm with a shoulder at 440 nm, while those of **TM2** exhibited characteristic peaks at 368 and 389 nm, respectively. **TM3** had a broad structureless emission with a λ_{max} at 408 nm. The PL spectra of our twin molecules in film states behaved differently. We observed that the PL maximum peaks both in solutions and

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(12) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(13) Yu, W.-L.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem. Commun.* **1999**, 1837.

(14) Nguyen, P.; Todd, S.; van den Biggelaar, D.; Taylor, N. J.; Marder, T. B.; Wittmann, F.; Friend, R. H. *Synlett.* **1994**, 299.

(15) Chow, H.-F.; Wan, C.-W.; Low, K.-H.; Yeung, Y.-Y. *J. Org. Chem.* **2001**, *66*, 1910.

(16) Blanchard, P.; Brisset, H.; Illien, B.; Riou, A.; Roncali, J. *J. Org. Chem.* **1997**, *62*, 2401.

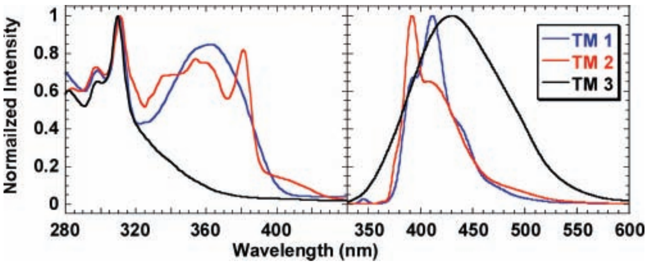

Figure 2. Normalized absorbance (left) and fluorescence (right) spectra of twin molecules **TM1−3** in film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

in films of **TM1** were quite close. **TM1** peaked at 394 and 412 nm with a shoulder at about 440 nm. This implied that intermolecular $\pi-\pi$ aggregation was substantially suppressed and **TM1** might form good amorphous states in films, which was attributed to the existence of both the large truxene and the 9,9′-spirobifluorene moieties. The PL spectrum of **TM1** also exhibited a narrow full width at half-maximum (fwhm) for about 50 nm, which indicated that **TM1** could be a good candidate for blue light-emitting materials. **TM2** presented a significant red shift to 392 and 409 nm. **TM3** also exhibited considerable red shift from 408 to 431 nm. The preliminary investigation of photophysical properties indicated that the properties of the twin molecules were strongly affected by the π-linkages.

In conclusion, we have developed a series of π-conjugated twin molecules **TM1−3** by connecting two truxene halves via a π-linkage. 9,9′-Spirobifluorenylene, ethynylene and vinylene groups connecting both truxene moieties, the large steric chromophere, play a key role on the properties of desired materials. The investigation of optical properties of **TM1−3** by UV−vis and photoluminescent spectroscopy demonstrates that the optical properties of the twin molecules are strongly affected by the π-linkages. The investigation indicates that **TM1** and **TM2** might be potential candidates for blue light-emitting materials. We have developed a platform to understand photophysical properties of conjugated polymers through the investigation of their corresponding twin molecules.

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Supporting Information Available: Experimental procedures, additional data, and details. This material is available free of charge via the Internet at http://pubs.acs.org.

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