Unusual fluorescene emission from ethynyltriphenylene-substituted diacetylenic molecular hinge. Formation of intramolecular excimer†

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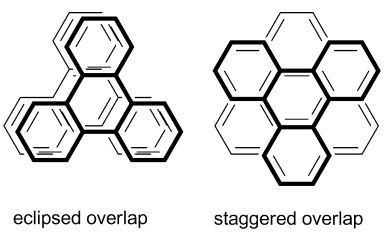
A diacetylenic molecular hinge bearing two ethynyltriphenylene units (**1**) has been synthesized. Evidence from ^{1}H NMR and variable temperature NMR (VT-NMR) of **1** in comparison to model compounds bearing only one triphenylene unit suggests that there is an equilibrium between the open conformer and the intramolecularly π–π interacting closed conformer in solution (equilibrium constant $K = 6.5$ at 298 K in $CDCl_3$) arising from the rotation of the diacetylenic hinge. Unusual fluorescence emission observed from **1** has been assigned to excimer formation arising from intramolecularly π–π interacting triphenylene units in the excited state. Steady state and picosecond time resolved fluorescence spectra of **1** were nearly identical and corresponded to intramolecular excimer emission.

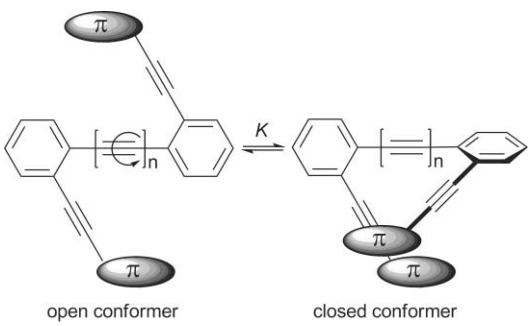
Introduction

It is well known that many aromatic molecules form excimers following electronic excitation and then emit from the excimer state at a longer wavelength compared to the monomer emission.[1] Excimer emission is generally observed at high concentrations. Pyrene is a typical example of such a molecule that readily emits from the excimer state at concentrations $>10^{-3}$ M.[1,2] However, there are few polycyclic aromatic molecules that do not form an excimer in the excited state and hence emission from the excimer state is very rare.[3] Triphenylene is a good example of such a molecule. Triphenylene and its derivatives do not emit from the excimer state even at high concentrations,[3,4] except when they are present in a constrained environment. Recently, excimer emission of a triphenylene derivative has been reported from a gel state.[5] Depending upon the type of overlap in the excited state, two types of excimer emissions have been suggested, one from the eclipsed overlap and the other from the staggered overlap (Scheme 1).[5] Emission from the solid state of triphenylene can also be considered as excimer emission due to extensive ground state intermolecular interactions in the crystalline state.



Scheme 1 Two types of overlap of triphenylene in the excimer state.

We have been interested in studying π-stacking interactions in molecular systems where large aromatic units are connected through an ethynyl bridge to a rigid acetylenic hinge (Scheme 2).[6] We address the question of whether or not π-stacking interactions would lead to the stabilization of certain conformers, such as the closed conformer in Scheme 2, in solution phase. Earlier we had used a pyrene chromophore to study π-stacking interactions.[6,7] We have reported the crystal structures of both the closed π-stacked conformer and the open conformer arising out of rotation of the diacetylenic hinge. (Scheme 2, π = pyrene, $n = 2$). *Ours is the first example of structural characterization of conformational isomers arising out of the rotation of a diacetylenic hinge*.[7] We have attributed the stability of the closed conformer to the π-stacking interaction of the two pyrene units.



Scheme 2 Conformational equilibrium of an acetylenic molecular hinge in open and closed forms.

In the present study we have made use of the same rigid diacetylenic molecular hinge[8] with triphenylene instead of pyrene (Scheme 3). The present study is aimed at studying the fluorescence emission of **1**, in particular emission from the intramolecular excimer state of triphenylene as it is very uncommon to observe excimer emission from triphenylene. In the present context the intramolecular excimer state corresponds to the two triphenylene units coming closer in the excited state as a result of rotation of the diacetylene hinge. As an extension of our earlier work on the pyrene derivatives we also address the question of whether the closed conformer is present in the ground state in equilibrium with the open form (Scheme 2). We probe the excited state using steady

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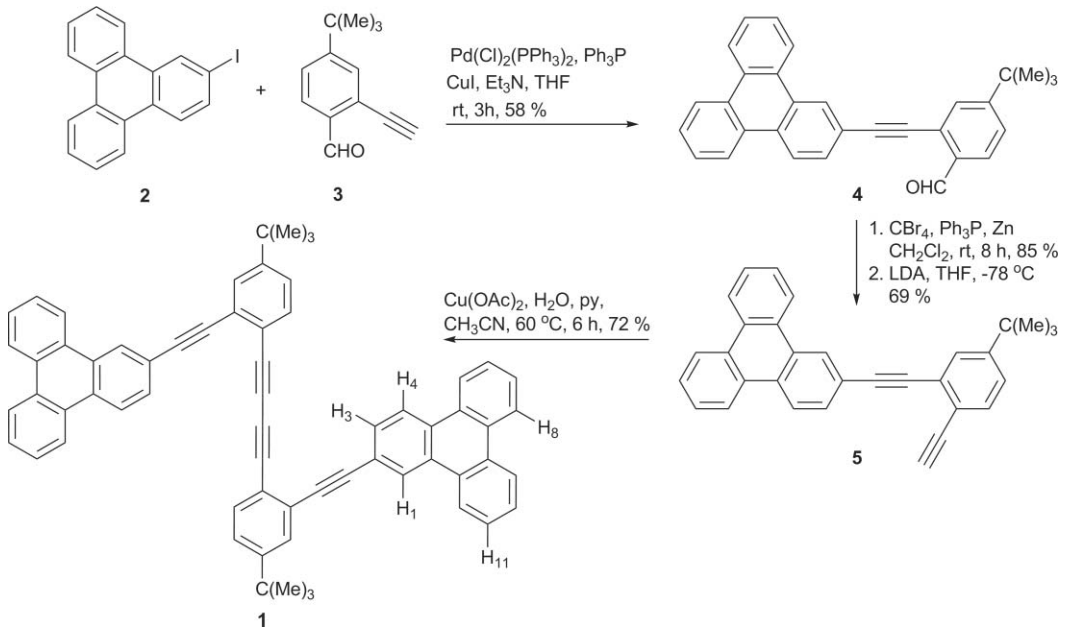
† Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR of all the synthesized compounds, ^{1}H–^{1}H COSY NMR of **1** and **5**, time resolved decay curves, temperature dependent fluorescence. See DOI: 10.1039/b923441a



Scheme 3 Synthesis of target **1**.

state and time resolved fluorescence spectroscopy and the ground state using NMR spectroscopy.

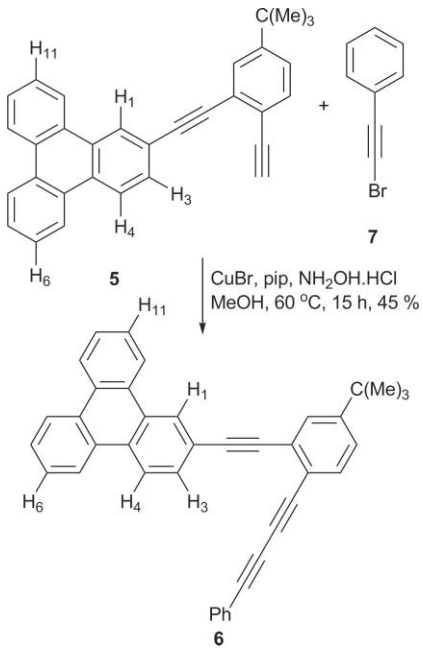
Results and discussion

Synthesis

Synthesis of target **1** was accomplished in 4 steps. Sonogashira coupling of 2-iodotriphenylene (**2**) and 4-*t*-butyl-2-ethynylbenzaldehdye (**3**) yielded **4** in 58% isolated yield. Conversion of **4** to terminal acetylene **5** was accomplished using the Corey–Fuchs method[9] in an overall yield of 59%. Oxidative coupling[10] of terminal acetylene **5** yielded the desired product (**1**) in 72% yield (Scheme 3). Target **1** was characterized by various spectroscopic data. Compound **6** with only one triphenylene unit was used as a model compound. It was synthesized by the Cadiot–Chadkiewicz coupling[11] of bromoethynylbenzene (**7**) with **5** (Scheme 4). For the sake of convenience numbering of the triphenylene ring protons is shown in Scheme 4.

Comparison of ^{1}H NMR spectra of 1 and model compounds

In triphenylene the bay region protons (H1, H4, H5, H8, H9, H12) appear at 8.5–8.6 ppm and the non-bay region protons (H2, H3, H6, H7, H10, H11) at δ 7.6–7.7 ppm. In **5** one of the bay region protons (H1) appeared at 8.87 ppm as a doublet (J 1.4 Hz), more deshielded than the rest due to the anisotropic effect of the adjacent acetylenic bond (Fig. 1). Similarly H3, a non-bay region proton adjacent to the acetylenic bond, appeared at 7.83 ppm (dd, J 8.6 and 1.4 Hz), more deshielded than the rest of the non-bay region protons. In case of **6**, protons H1 and H3 appeared at slightly higher chemical shift values than that of **5** at 8.95 and 7.89 ppm, respectively, due to an increase in conjugation (Fig. 1). The aromatic region of the ^{1}H NMR spectra of **1**, **5** and **6** is compared in Fig. 1. It is evident that protons of **1** are more shielded by about 0.4 ppm than those of **5** and **6**. It is also



Scheme 4 Synthesis of model compound **6** with one triphenylene unit.

evident that **1** should possess a symmetrical structure (presumably a C_2 axis) resulting in the chemical equivalence of a given proton in one triphenylene ring to that of the same proton on the other ring. Furthermore, the proton resonances in **1** are more resolved and spread out than those of **5** and **6**. For example, two of the bay region protons, namely H4 and H5, are well resolved and appeared at 8.13 and 8.0 ppm as doublets, respectively. One of the non-bay region protons, H6, is the most shielded one and appeared at 7.22 ppm as a triplet. H1 appeared at 8.5 ppm as a doublet. These assignments are based on a careful analysis of the ^{1}H–^{1}H COSY spectra of **1** and **5**. In the absence of any π–π interaction between the triphenylene units in **1** the chemical

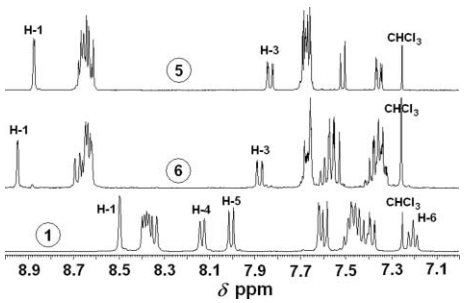


Fig. 1 Comparison of the aromatic region of the ^{1}H NMR spectra of **5** (top), **6** (middle) and **1** (bottom) in $CDCl_3$ at 25 °C.

shift of the triphenylene ring protons would have been either same as that of **6** or slightly more deshielded than **6** due to further increase in conjugation. However, a reverse trend is observed for **1**. The shielding of the protons of **1** compared to those of **5** and **6** is due to intramolecular π-stacking interaction of the two triphenylene units in **1**. π-Stacking usually results in the shielding the protons in ^{1}H NMR spectrum due to ring current effect of the aromatic rings.[12,13] The spreading out of resonances is due to shielding of different protons to different extents depending on their placement in the ring current effect.[14] *In the absence of any heteroatom substituents exerting strong electronic effects the shielding of protons of* ***1*** *compared to* ***5*** *and* ***6*** *as well as enhanced resolution of the ring protons in* ***1*** *compared to* ***5*** *and* ***6*** *could only be explained on the basis of π-stacking and consequent ring current effect of one triphenylene ring on the proton chemical shifts of the other*.

Variable temperature ^{1}H NMR (VT-^{1}H NMR) studies of 1

The question of whether or not **1** exists as an equilibrium mixture of the open and closed forms as shown in Scheme 2 in the ground electronic state with π–π interactions between the triphenylene moieties in the closed form is conveniently studied by ^{1}H NMR spectroscopy. The chemical shifts of aromatic protons are sensitive to π–π interactions.[12–14] Typically, aggregation due to π-stacking results in the shielding of aromatic proton resonances resulting in lower chemical shift values due to an aromatic ring current effect. At any given temperature NMR would give the average chemical shift arising out of the equilibrium in Scheme 2. *It should be emphasized here that the ^{1}H NMR spectra of the model compounds* ***5*** *and* ***6*** *with only one triphenylene unit were independent of temperature of measurement*. Being a weak molecular interaction (interaction energy is about 2–10 kJ mol^{-1})[15] π–π interaction is perturbed by temperature. An increase in temperature generally results in breaking of the π–π interactions. A systematic investigation of the effect of temperature on the ^{1}H NMR spectrum of **1** was undertaken in the temperature range of 298 to 408 K in $CDCl_2CDCl_2$. Upon increasing the temperature the chemical shift of various triphenylene protons increased gradually (Fig. 2). For example the chemical shift of H1, H4, H5 and H6, increased from δ 8.45, 8.09, 7.99, 7.14 ppm, respectively, at 298 K to δ 8.58, 8.21, 8.13, 7.25 ppm, respectively, at 408 K. The effect of increasing temperature on the chemical shift of H4 and H5 is shown in Fig. 3, and a similar trend was observed for H1 and H6. It should be noted that in this temperature range the chemical shifts of the phenyl protons remained unchanged (Fig. 2). As the temperature

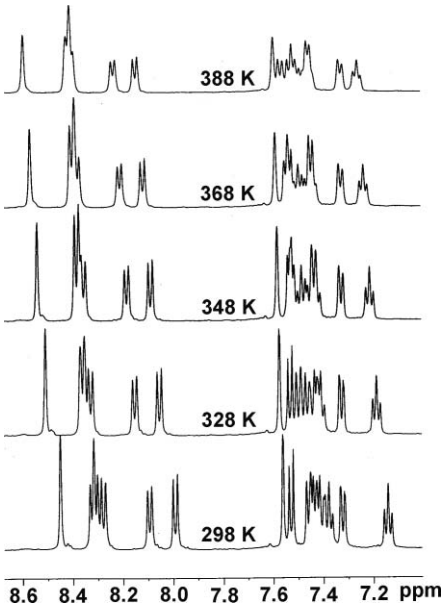


Fig. 2 VT-^{1}H NMR spectra of **1** in $CDCl_2CDCl_2$. Only the aromatic region is shown.

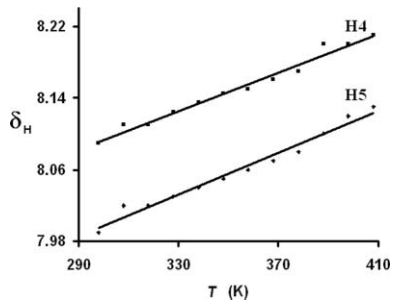


Fig. 3 Effect of temperature on the chemical shift of H4 and H5 protons in **1**.

is raised, the intramolecular π–π interaction is disturbed and as a consequence the chemical shift of various protons increased (Fig. 2). The observed chemical shifts are only an average of the open and closed forms of **1**. With increasing temperature the population of open is increased in the equilibrium (Scheme 2) and hence the chemical shifts of various hydrogens are increased. Thus, the ^{1}H NMR data clearly supports the existence of the equilibrium between the open and closed forms of **1** in the solution phase. The chemical shift of triphenylene protons in the model compounds **4** and **5** could be taken as equal to the open form of **1** (devoid of π–π interactions). The poor solubility of **1** hampered measurement of NMR below 298 K in $CDCl_2CDCl_2$. Therefore, low temperature measurements were made in $CDCl_3$ in the temperature range of 233–298 K (ESI, Fig. S24†). As the temperature is lowered the chemical shift of various triphenylene protons decreased until 253 K. Below this temperature the chemical shift of various protons were invariant. The chemical shift of H1 proton remained at 8.43 ppm below 253 K.

As an approximation, the chemical shift of H1 in **1** at 233 K was taken as that of the closed form. The chemical shift of H1 in the model compound **6** was taken as that of the open form. Using these values the equilibrium constant K as given in Scheme 2 was estimated to be 6.5 at 298 K in $CDCl_3$ (ESI†). This

value is comparable to that reported earlier for the corresponding pyrene derivative from our laboratory.[7] Using VT-NMR data the thermodynamic parameters for the equilibrium were estimated ($\Delta G = -4.6$ kJ mol^{-1}, $\Delta H = -14.2$ kJ mol^{-1} and $\Delta S = -32.2$ J mol^{-1} K^{-1} in $CDCl_3$) (ESI†).

Absorption and fluorescence emission studies

A comparison of the absorption spectra of **1**, **5** and **6** in cyclohexane is shown in Fig. 4. Compared to the spectrum of **5** which has an absorption cut-off at 360 nm the bands of **1** and **6** are broader and more red shifted as expected due to extended conjugation. The additional broad band in the region 380–400 nm for **1** might be due to intramolecular π–π interaction arising from the closed form of **1**. This additional broad band in **1** in the longer wavelength region in comparison with the model compounds is reminiscent of the "cyclophane band" arising due to intramolecular π–π interaction in cyclophanes wherein the aromatic units exist within the distance of 3.2–3.5 Å when the bridge length is small.[16]

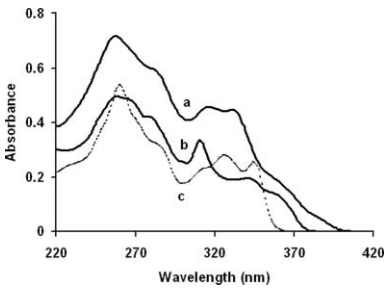


Fig. 4 Absorption spectrum of **1** (a), **6** (b) and **5** (c) (---) in cyclohexane (1×10^{-5} M).

In cyclohexane, triphenylene emits from the monomer state at 370 nm.[4] *It does not exhibit any excimer emission even in more concentrated solutions*. However, emission in the solid state at 408 nm could be attributed to excimer emission in view of the ground state π–π interactions in the solid state as revealed from the crystal structure of triphenylene.[17] Similarly for the model compound **5**, fluorescence emission occurred at 375 and 383 (sh) nm in CH_2Cl_2, and 432 nm in the solid state. Compared to triphenylene, both the absorption and emission bands of **5** are red-shifted due to extended conjugation of the phenylethynyl unit. The large bathochromic shifts of approximately 38–55 nm between the emission bands in solution state and in solid state, respectively, of triphenylene and **5** are due to emission from the monomer state in solution and from the excimer state in solid. In the case of **1**, fluorescence emission in cyclohexane showed two bands at 411 (sh) and 438 nm (Fig. 5). Emission in the solid state was only slightly red-shifted by 5 nm and appeared at 443 nm as a broad featureless band. Compared to **5** and **6**, emission of **1** in solution phase is red-shifted by 50 nm. The fluorescence emission of **1** was independent of concentration as well as the excitation wavelength (ESI, Fig. S1 and S2†). The emission spectrum of **1** in solution phase is very similar to the excimer emission of a triphenylene derivative reported in the gel state with two bands.[5] Based on spectral comparison we conclude that the two triphenylene units are π-stacked in a staggered manner (Scheme 1). π-Stacking of the two triphenylene units in a staggered manner gives two emission

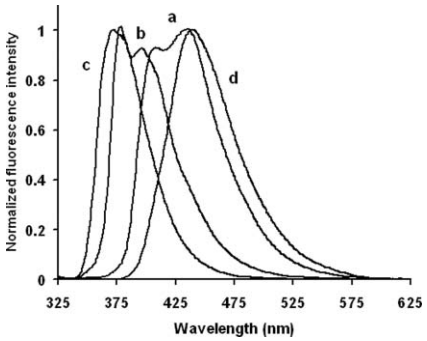


Fig. 5 Fluorescence emission spectrum of **1** (**a**) ($\phi_f = 0.10$), **6** (**b**) ($\phi_f = 0.14$) and **5** (**c**) ($\phi_f = 0.19$) in cyclohexane (1×10^{-5} M) and **1** (**d**) in the solid state. $\lambda(ex) = 310$ nm.

bands in the region 400–450 nm. Emission from eclipsed overlap of the two triphenylene units gives red-shifted emission around 550 nm.[5] Our results are consistent with staggered overlap of the two triphenylene units in the closed conformer (Scheme 2). Furthermore, the fluorescence emission was measured within the narrow temperature range of 283–343 K (ESI, Fig. S3†). Systems that undergo ground state π-stacking usually show a small blue shift in the emission wavelength at higher temperatures due to the disruption of the π-stacking interactions. Our observations are consistent with the observations in the literature[18] in that the fluorescence emission was shifted from 438 nm at 283 K to 433 nm at 343 K (ESI, Fig. S3†). These observations based on the absorption and fluorescence emission data further support the presence of equilibrium shown in Scheme 2 in solution. Considering that the barrier for rotation along the diacetylenic bond in **1** is very low, emission from the excimer state of **1** where the two triphenylene units come close (as in the closed form in Scheme 2) is reasonable. The excimer emission of **1** arises from the closed form that exists in the ground state of **1** in addition to the excimer formed in the excited state by the rotation of the diacetylenic axis. The fluorescence quantum efficiencies (ϕ_f) of **1**, **5** and **6**, respectively, are 0.10, 0.19 and 0.14 in cyclohexane. They were measured using 9.10-diphenylanthracene as the standard.[1]

Time resolved fluorescence studies

The time resolved fluorescence spectrum of **1** was recorded, and the fluorescence lifetimes of **1** and **5** were also measured using the picosecond time correlated single photon counting (TCSPC) technique. The time resolved fluorescence spectrum of **1** measured in cyclohexane is shown in Fig. 6 and it closely resembled the steady spectrum (Fig. 5) with two maxima at 400 and 431 nm. The time resolved fluorescence spectrum was also reminiscent of the excimer spectrum of triphenylene derivative reported in the literature.[5] The spectrum corresponds to excimer emission arising from the staggered π-stacked triphenylene units in the closed form. It should be noted that under the picosecond time regime of measurement the monomer emission spectrum of **1** was not observed, rather the excimer emission spectrum was directly observed.

The fluorescence lifetime measurements for **1** and **5** were made in cyclohexane using a diode laser as the excitation source at 266 and 280 nm with a pulse width of 50 and 150 ps, respectively. The monomer fluorescence decay of **5** observed at 375 nm followed a clean first order decay and the fluorescence life time was 10.3 ±

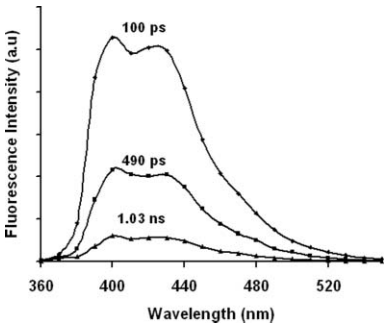


Fig. 6 Time resolved fluorescence emission spectra of **1** measured in cyclohexane after 100 ps, 490 ps and 1.03 ns delay after the laser excitation at λ (ex) = 266 nm, pulse width = 50 ps.

0.1 ns, as expected (ESI, Fig. S22†).[5] The excimer fluorescence decay of **1** was followed at 406 and 436 nm (ESI, Fig S23†). The decay profile was nearly identical at both the wavelengths. The decay of excimer emission of **1** at these two wavelengths followed a more complex kinetics presumably due to many conformational isomers (open and closed forms shown in Scheme 2 are the two extreme cases) and could be fitted to only biexponential decay. The decay was too fast compared to that of **5**. An approximate estimate of the lifetime of the excimer emission of **1** is about 0.39 ns.

Conclusions

We have synthesized a molecular hinge (**1**) with ethynyltriphenylene units as pendant groups. Evidence from ^{1}H NMR and VT-NMR of **1** suggest that there is an equilibrium between the open conformer and the intramolecularly π–π interacting closed conformer in solution. The extra band observed in the electronic spectrum of **1** at longer wavelengths in comparison to the model compounds **5** and **6** is indicative of π–π interaction between the triphenylene units in the ground state. Observation of a longer wavelength broad band is reminiscent of such bands in cyclophanes where the aromatic units are held face-to-face[16] within π-stacking distance. Fluorescence spectroscopy also revealed unusual excimer emission from **1**, unusual because triphenylene moiety is known to emit from the excimer state only under constrained environment. The observed spectrum is reminiscent of the excimer emission spectrum reported for another triphenylene derivative in the literature.[5] In the closed conformer, the two triphenylene units are intramolecularly π-stacked in a staggered manner as evident from the comparison of fluorescence spectrum with the literature.[5] The steady state and the time resolved picosecond fluorescence spectra of **1** were nearly identical. Based on the NMR (electronic ground state) and UV-Vis and fluorescence (electronic excited state) spectroscopic data we conclude that in molecular hinge **1**, the closed conformer with the two triphenylene units with π-stacking interactions is present in equilibrium with the open form.

Experimental

General experimental methods[19] and instrumentation for time resolved fluorescence spectrum and decay measurements[20] have been published elsewhere. The solutions were thoroughly degassed by purging either dry nitrogen or dry argon prior to the fluorescence measurements. Steady state fluorescence spectra were measured on a Hitachi F4500 spectrometer.

2-Iodotriphenylene (2)

To a suspension of triphenylene (300 mg, 1.31 mmol) in acetic acid (50 mL), water (5 mL) and sulfuric acid (0.5 mL) was added iodine (200 mg, 0.79 mmol) and potassium iodate (68 mg, 0.32 mmol). The reaction mixture was heated at 55 °C for 1 day. It was cooled to room temperature and poured into water (100 mL). The mixture was extracted with CH_2Cl_2 (100 mL) and the organic layer was washed with sodium thiosulfate solution (2 × 50 mL) and finally with water (100 mL). It was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure to give a pale brown solid. It was purified by column chromatography over silica gel using hexane to give a colorless solid (360 mg) which contained an inseparable mixture of 2-iodotriphenylene and triphenylene (45 : 55). The mixture was used as such for further reaction. A small amount (100 mg) of the mixture was purified by column chromatography and pure 2-iodotriphenylene was characterized by ^{1}H and ^{13}C NMR spectroscopy. (*Note: use of excess iodinating agent resulted in the formation of a mixture of mono and polyiodotriphenylenes which were inseparable*). δ_H (400 MHz, $CDCl_3$) 8.93 (d, *J* 1.6 Hz, 1 H, 1-H), 8.51-8.63 (m, 4 H), 8.31 (d, *J* 8.4 Hz, 1 H, 4-H), 7.89 (dd, *J* 1.6, 8.4 Hz, 1 H, 3-H), 7.62-7.69 (m, 4H) ppm. δ_C (100 MHz, $CDCl_3$) 135.79, 132.48, 131.75, 129.99, 129.79, 129.16, 129.06, 128.37, 127.81, 127.69, 127.42, 127.39, 125.03, 123.37, 123,33, 123.30, 123.07, 93.31 ppm; *m/z* [%] MALDI-TOF MS calcd for $C_{18}H_{11}I$, 354; found 354 [M^+, 100], 355 [M^++1, 40]; 356 [M^++2, 10].

2-(5-*tert*-Butyl-2-formylphenylethynyl)triphenylene (4)

A Schlenk flask was charged with a mixture of 2-iodotriphenylene and triphenylene (1 : 1 mole ratio) (4.66 g), $Pd(PPh_3)_2Cl_2$ (208 mg, 0.30 mmol), PPh_3 (155 mg, 0.60 mmol), CuI (113 mg, 0.60 mmol), degassed THF (60 mL) and Et_3N (60 mL). The reaction mixture was stirred at room temperature for 15 min and 4-*tert*-butyl-2-ethynylbenzaldehyde (1.0 g, 5.38 mmol) was added. Stirring was continued for 3 h at room temperature. The solvent was removed and the residue was dissolved in CH_2Cl_2 (200 mL). The solution was washed with 5% aqueous HCl solution (2 × 100 mL) and finally with water (100 mL). It was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The crude product was purified by column chromatography over silica gel. Elution with hexane yielded triphenylene followed by elution using a mixture of hexane and CH_2Cl_2 (90 : 10, v/v) yielded **4** as a colorless solid (1.28 g, 58%). Mp 75–77 °C. IR (neat) 2206 (C≡C), 1689 (C=O) cm^{-1}. δ_H (400 MHz, $CDCl_3$) 10.72 (s, 1 H, CHO), 8.80 (d, *J* 1.6 Hz, 1 H, 1-H), 8.56-8.64 (m, 5 H), 7.94 (d, *J* 8.4 Hz, 1 H, 4-H), 7.76 (dd, *J* 1.6 and 8.4 Hz, 1 H, 3-H), 7.74 (d, *J* 1.6 Hz, 1 H, 3-H phenyl), 7.62-7.68 (m, 4 H), 7.52 (dd, *J* 1.6 and 8.0 Hz, 1 H, 4-H phenyl), 1.42 (s, 9 H, $C(Me)_3$) ppm. δ_C (100 MHz, $CDCl_3$) 191.40 (CHO), 157.82, 133.69, 130.22, 130.17, 130.07, 129.99, 129.76, 129.16, 128.94, 127.76, 127.69, 127.41, 127.37, 127.34, 126.97, 126.64, 126.21, 123.55, 123.38, 123.36, 123.31, 121.02, 96.04 (C≡C), 86.33 (C≡C), 35.34, 30.97 ppm; *m/z* [%] ESI Q-TOF MS 413 [M^++1] (100). HRMS calcd. for $C_{31}H_{25}O$ [M + H^+] 413.1905; found 413.1904.

2-(5-*tert*-Butyl-2-ethynylphenylethynyl)triphenylene (5)

To a solution of PPh_3 (2.033 g, 7.76 mmol) in dry CH_2Cl_2 (50 mL) zinc powder (578 mg, 7.76 mmol) was added and the reaction mixture was cooled to 0 °C. CBr_4 (1.288 g, 3.88 mmol) was added portionwise over 15 min. The reaction mixture was brought to room temperature and stirring was continued for 3 h. Aldehyde **4** (400 mg, 0.97 mmol) was added and stirring was continued for 8 h. The reaction mixture was filtered and the residue was washed with CH_2Cl_2. The washings along with the filtrate were evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using a mixture of hexane and CH_2Cl_2 (95 : 5, v/v) to yield a colorless solid which contained triphenylphosphine and the desired dibromovinyl derivative. The white solid was dissolved in CH_2Cl_2 (50 mL) and excess methyl iodide (5 mL) was added to form methyltriphenylphosphonium iodide. The mixture was stirred overnight. The solvent was removed and crude product was purified by column chromatography over silica gel using a mixture of hexane and CH_2Cl_2 (95 : 5 v/v) to yield the dibromovinyl derivative as a colorless solid (469 mg, 85%). **2-(5-*tert*-Butyl-2-(1,1-dibromovinyl)phenylethynyl)-triphenylene**. Mp: 80–82 °C. IR (neat) 2958, 2191 (C≡C) cm^{-1}. δ_H (400 MHz, $CDCl_3$) 8.86 (d, *J* 1.6 Hz, 1 H, 1-H), 8.62-8.68 (m, 5 H), 7.97 (s, 1 H), 7.78-7.82 (m, 2 H), 7.66-7.70 (m, 4 H), 7.42 (dd, *J* 2.4, 8.0 Hz, 1 H, 4-H phenyl), 1.38 (s, 9 H, $C(Me)_3$) ppm; δ_C NMR (100 MHz, $CDCl_3$) 151.63, 135.81, 134.53, 130.12, 130.01, 129.81, 129.78, 129.30, 129.14, 129.07, 127.75, 127.69, 127.64, 127.43, 127.40, 126.88, 125.56, 123.54, 123.42,123.39, 123.33, 122.46, 121.64, 94.99, 90.68, 88.64, 34.81, 31.10 ppm; *m/z* MALDI-TOF MS calcd for $C_{32}H_{24}Br_2$, 568; found 567 [M^+-1]. An oven dried Schlenk flask was charged with the dibromovinyl derivative (300 mg, 0.53 mmol) and dry THF (30 mL). The solution was cooled to −78 °C and LDA (1.59 mmol) [freshly prepared from *n*-BuLi (1.59 mmol, 1.3 mL of 1.2 M solution in hexane) and diisopropylamine (161 mg, 0.22 mL)] was added and stirring was continued for 1 h. Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution (20 mL) at −78 °C. The reaction mixture was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with water (2 × 30 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated to dryness and crude product was purified by column chromatography over silica gel using a mixture of hexane and CH_2Cl_2 (95 : 5, v/v) to yield **5** as a colorless solid (0.149 g, 69%). Mp 73–76 °C. IR (neat) 3283, 2958, 2222 (C≡C) cm^{-1}. UV-Vis (CH_2Cl_2) λ (log ε) 259 (4.726), 285 (4.503), 310 (4.348), 324 (4.442), 343 (4.340); δ_H NMR (400 MHz, $CDCl_3$) 8.87 (d, *J* 1.4 Hz, 1 H, 1-H), 8.61-8.68 (m, 5 H), 7.83 (dd, *J* 1.5, 8.6 Hz, 1 H, 3-H), 7.65-7.70 (m, 5 H), 7.51 (d, *J* 8.2 Hz, 1 H, 3-H phenyl), 7.35 (dd, *J* 2.0, 8.2 Hz, 1 H, 4-H phenyl) 3.40 (s, 1 H, acetylenic H), 1.36 (s, 9 H, $C(Me)_3$) ppm; δ_C NMR (100 MHz, CDCl3) 152.04, 132.45, 130.10, 129.99, 129.72, 129.69, 129.35, 129.14, 128.97, 127.61, 127.57, 127.36, 126.98, 125.89, 125.49, 123.52, 123.40, 123.36, 123.31, 121.95, 121.81, 93.26, 89.27, 82,44, 80.50, 34,85, 31.07 ppm; *m/z* [%] MALDI-TOF MS calcd for $C_{32}H_{24}$, 408; found 408 [M^+, 100], 409 [M^++1, 23], 410 [M^++2, 5].

Synthesis of 1

$Cu(OAc)_2 \cdot H_2O$ (486 mg, 2.44 mmol) was dissolved in acetonitrile (28 mL) and pyridine (7 mL) and **5** (250 mg, 0.61 mmol) was added. The reaction mixture was stirred at 60 °C for 6 h. It was cooled to room temperature and neutralized with 5% aq HCl solution (20 mL). The mixture was extracted with CH_2Cl_2 (2 × 20 mL) and the organic layer was washed with water (2 × 15 mL). The organic layer was dried over sodium sulfate and evaporated to dryness. The crude product was purified by column chromatography over silica gel using a mixture of hexane and CH_2Cl_2 (90 : 10, v/v) to yield **1** as a colorless solid (0.180 g, 72%). Mp 217 °C (decomp). IR (neat) 2957, 2866, 2190 cm^{-1}; UV-Vis (CH_2Cl_2): λ (log ε) 257 (5.044), 267 (5.048), 312 (4.795), 332 (4.771), 361 (4.494). δ_H NMR (400 MHz, $CDCl_3$) 8.50 (s, 1 H, 1-H), 8.33-8.40 (m, 3 H), 8.13 (d, *J* 8.0 Hz, 1 H, 4-H), 8.00 (d, *J* 8.6 Hz, 1 H, 5-H), 7.62 (d, *J* 1.6 Hz, 1 H), 7.59 (d, *J* 8.2 Hz, 1 H) 7.37-7.51 (m, 5 H), 7.20 (dd, *J* 7.3, 7.9 Hz, 1 H, 6-H), 1.40 (s, 9 H, $C(Me)_3$) ppm; δ_C NMR (100 MHz, $CDCl_3$) 152.51, 132.49, 129.80, 129.64, 129.53, 129.29, 129.22, 129.00, 128.88, 128.64, 127.33, 127,12, 126.99, 126.91, 126.83, 126.77, 125.35, 123.48, 123.20, 123.20, 122.88, 122.72, 121.96, 121.32, 94.70, 89.13, 81.63, 77.82, 34.98, 31.08 ppm; *m/z* MALDI-TOF MS calcd for $C_{64}H_{46}$, 814; found 813 [M^+-1].

Synthesis of model compound 6

To a stirred solution of a mixture containing **5** (15 mg, 0.03 mmol), piperidine (3.74 mg, 0.044 mmol), CuBr (0.28 mg, 0.002 mmol), and hydroxylamine hydrochloride (2.08 mg, 0.03 mmol) in methanol (10 mL) under nitrogen atmosphere at room temperature was added a degassed solution of phenylbromoethyne (**7**, 8.0 mg, 0.04 mmol) in methanol (3 mL) over a period of 15 min. The mixture was stirred for 3 h at room temperature and then heated for 15 h at 60 °C. Solvent was removed under reduced pressure in the rotary evaporator, and the crude product was poured into ice cold water (10 mL) and extracted with dichloromethane (2 × 5 mL). The organic extract was washed with saturated brine solution (5 mL). The organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude product was purified by column chromatography over silica gel using a mixture of hexane and CH_2Cl_2 (95: 5, v/v) to yield **6** as a white solid (8 mg, 45%). In this reaction the dimer (**1**, 7 mg) was also isolated. **6**: Mp: 169–171 °C. IR (neat) 2961, 2867, 2216 (C≡C) cm^{-1}. δ_H NMR (500 MHz, $CDCl_3$) 8.95 (d, *J* 1.0 Hz, 1 H, 1-H), 8.63-8.70 (m, 5 H), 7.89 (dd, *J* 2, 9.0 Hz, 1 H, 3-H), 7.67-7.69 (m, 3 H), 7.55-7.61 (m, 4 H), 7.34-7.41(m, 5 H) 1.35 (s, 9 H, $C(Me)_3$) ppm; δ_C NMR (100 MHz, $CDCl_3$) 152.52, 132.68, 132.51, 130.12, 130.02, 129.92, 129.77, 129.74, 129.34, 129.22, 129.12, 128.76, 128.46, 127.62, 127.49, 127.43, 127.35, 126.77, 125.57, 123.55, 123.45, 123.42, 123.36, 123.21, 121.93, 121.83, 121.73, 94.10, 89.22, 82.39, 80.62, 74.34, 34.98, 31.04 ppm; *m/z* MALDI-TOF MS calcd for $C_{40}H_{28}$ 508; found 508 [M^+, 100%], 509 [M^++1, 30%], 510 [M^++2, 5%], 493 [M^+-CH_3, 10%].

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