



Synthesis of a triethylene glycol-capped benzo[1,2-*c*:4,5-*c'*]bis[2]benzopyran-5,12-dione: A highly soluble dilactone-bridged *p*-terphenyl with a crankshaft architecture



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ABSTRACT

3,10-Bis(triethylene glycol)benzo[1,2-*c*:4,5-*c'*]bis[2]benzopyran-5,12-dione has been synthesized as an example of a dilactone-bridged *p*-terphenyl with a C_{2h} crankshaft architecture that exhibits significant fluorescence. Lactone-bridged rotationally restricted *p*-terphenyl compounds are relatively unexplored, with the few known examples having very poor solubility and are therefore difficult to characterize and study. This superior TEG-solubilized analog has been shown to have much improved solubility, which should improve processability, and has attractive optical properties including efficient absorption in the near UV and significant emission of blue-violet light. Studies enabled by this TEG-solubilized crankshaft shaped molecule establishes that compounds with this architecture could be useful as pH-driven molecular switches with limited switching cycles or as “turn-off” sensors with instant fluorescence and UV absorption attenuation at high pH values.

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Introduction

Biphenyl, *p*-terphenyl, and other linear oligophenyl-containing conjugated materials have long been studied for their interesting optical properties (Fig. 1) [1]. These properties are intimately connected to certain structural characteristics of the phenyl-containing molecules, specifically the number of individual conjugated arene units and their torsional angle relative to one another [2]. It is known that increasing the number of conjugated arene units in unsubstituted oligo(*p*-phenylenes) causes a bathochromic shift in both absorbance and emission spectra, coupled with an increase in fluorescence quantum yield (Φ_F) [2b]. However, there is a general convergence observed for these types of systems after which additional benzene units (typically around 4 total units) have minimal effect on these properties. In oligophenylenes with terminal donor–acceptor (D–A) units this convergence is often realized more rapidly, sometimes even resulting in a hypsochromic shift in absorption spectra, as the cumulative phenyl–phenyl torsions become increasingly dominant, thus disrupting electronic communication between the D–A end groups [2c,2d]. A solution to this issue is to engineer bridging units between the individual arenes that will restrict aryl–aryl torsional motion, allowing for efficient

π -conjugation between the arene units. As an example of this effect (Fig. 1), biphenyl (dihedral angle in solution is 30–40°) [3] is a fluorescent molecule with a $\Phi_F = 0.18$ [4]. When biphenyl is bridged by a single methylene unit as in 9*H*-fluorene, restricting the aryl–aryl torsions, it becomes especially fluorescent ($\Phi_F = 0.80$) [4]. Because of these enhanced optical properties, bridged oligo(*p*-phenylene) chromophores, such as indeno[1,2-*b*]fluorene and derivatives, and larger poly(*p*-phenylene) chromophores have found utility in organic electronic devices such as polymer lasers, organic light-emitting diodes (OLEDs), and solar cells [5]. One of the key areas of interest for the oligomeric compounds is in the creation of stable blue light emitters for OLED applications [6]. However, a major drawback of both bridged and non-bridged oligo(*p*-phenylenes) is their poor solubility due to strong intermolecular π – π stacking interactions. This leads to aggregation which alters key optical properties and causes difficult characterization and processing [7]. Most significantly, aggregation often diminishes light emission, which can be attributed to non-radiative relaxation via energy transfer between aggregated species. The issue of aggregation is most conveniently addressed in methylene bridged oligo(*p*-phenylene) or poly(*p*-phenylene) structures by the incorporation of alkyl or aryl solubilizing groups along the methylene backbone, allowing for the facile synthesis of a myriad of interesting variations on these types of structures in recent years [8].

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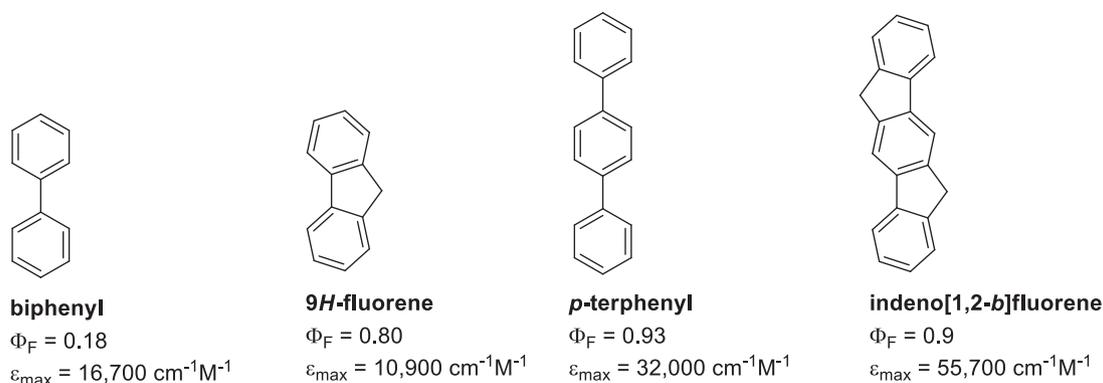


Fig. 1. Reported solution-phase electronic absorption and emission efficiency for small bridged and unbridged *p*-phenylenes in cyclohexane [4].

We have been interested in exploring a unique bridging group to restrict aryl-aryl rotation and therefore augment π -conjugation in biphenyl and oligophenylene molecules: the lactone unit [9]. We have demonstrated that donor-acceptor functionalized biphenyls with a lactone bridge have attractive optical properties which are enhanced relative to non-bridged analogs [9a]. Additionally, unlike other common bridges, we have shown that lactone bridges have the unique potential to function as pH-driven aryl-aryl dihedral angle molecular switches through the reversible base-promoted cleavage and acid-promoted reformation of the lactone bridge, reversibly affecting their optical properties [9a,9b]. Although compounds containing a biphenyl unit with a lactone bridge, *i.e.* benzocoumarins, are fairly common [10], applying multiple lactone bridges to larger oligophenylene-containing compounds is quite rare. In previous work, we have reported the synthesis of some of the only known examples (Fig. 2) of dilactone-bridged *p*-terphenyls with C_{2h} symmetric or “crankshaft” architectures [9b] (benzo[1,2-*c*:4,5-*c'*]bis[2]benzopyran-5,12-diones **2** and **3**, and benzo[1,2-*c*:4,5-*c'*]bis[1]benzopyran-6,13-dione **5**) and trilactone-bridged 1,3,5-triphenylbenzenes with C_{3h} symmetric or “triskelion” architectures [9c] (benzo[*c*]diisochromeno[3,4-*f*:3',4'-*h*]chromene-6,12,18-triones **6** and **7**). Beyond these studies, there are only a few known examples of crankshaft shaped dilactone-bridged *p*-terphenyls [11] and no examples of triskelion shaped lactone-bridged 1,3,5-triphenylbenzenes. Unsubstituted dilactone-bridged *p*-terphenyl compounds benzo[1,2-*c*:4,5-*c'*]bis[2]benzopyran-5,12-dione **1** [11a] and benzo[1,2-*c*:4,5-*c'*]bis[2]benzopyran-6,13-dione **4** [11b], isomeric via the flipping of the two lactone bridging units, are known but have very poor solubility. Unsubstituted trilactone-bridged 1,3,5-triphenylbenzene (6*H*-benzo[*c*]diisochromeno[3,4-*f*:3',4'-*h*]chromene-6,12,18-trione) is currently unknown, although we had previously attempted its synthesis to find that it was completely insoluble in all solvents and were therefore unable to fully characterize this compound [9c]. We attempted to address the solubility issues caused by the intense π - π intermolecular forces of these compounds by installing *t*-butyl [9b,9c] (**2**, **5**, **6**), 3,5-di-*t*-butylphenyl [9b] (**3**), and 1,1,4,4-tetramethylbutylene [9c] (**7**) groups. Each of these groups are commonly employed to solubilize planar conjugated materials [12]. While these solubilizing groups did successfully allow for solution-phase characterization of these compounds, their solubility was still very poor and limited to only a few solvents, sometimes requiring heat to dissolve: CH_2Cl_2 , CHCl_3 , toluene, and THF (in some cases) [9b,9c]. While some of these compounds had very attractive optical properties, their poor solubility would be an issue for the processing of these compounds for potential application in optical devices. Another issue caused by their poor solubility is that the pH-driven molecular switch potential of these larger lactone-bridged compounds could not be examined fully due to the precip-

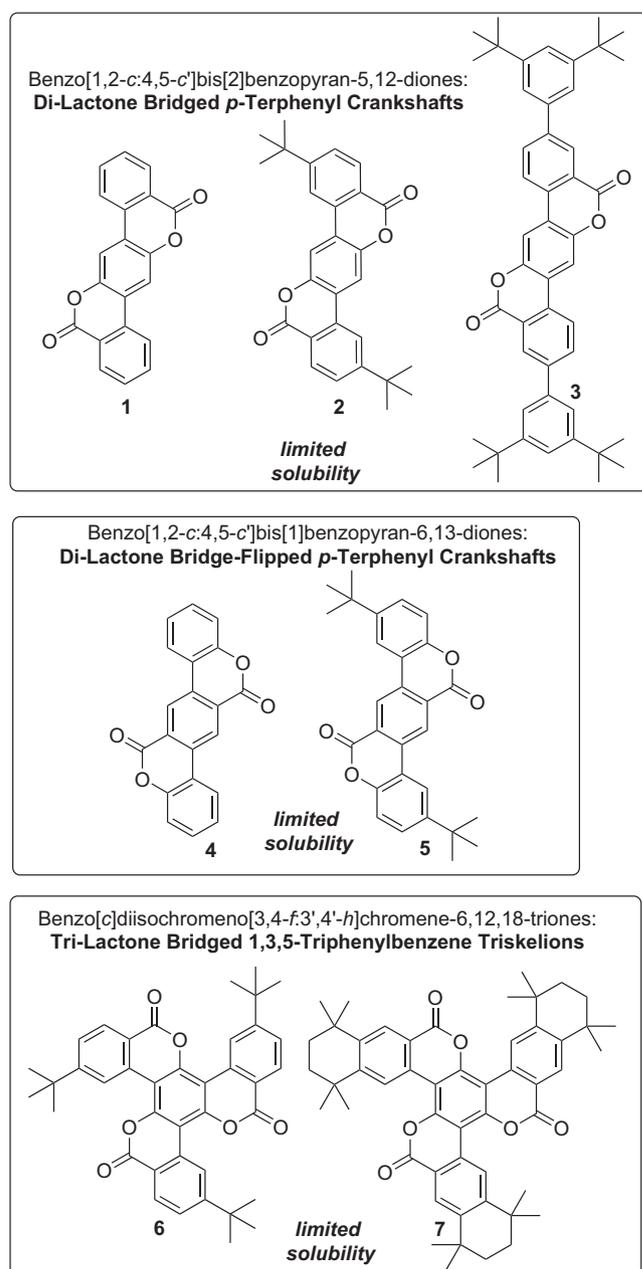


Fig. 2. Examples of lactone-bridged oligo(*p*-phenylene)s with limited solubility.

itation that occurred after the introduction of switching stimuli [9b,9c].

We sought to incorporate a new solubilizing group into these rare classes of compounds which would allow for more favorable processing for optical applications and the demonstration of their pH-driven switch capabilities. Of all the compounds in Fig. 2, crankshaft **2** and **3** had the most desirable optical properties, so we prioritized the synthesis of a soluble analog of those compounds. Oligoethylene glycol solubilizing groups are well-known for their ability to solubilize conjugated aromatics in polar solvents [13]. Other common solubilizing groups employed for these purposes include carboxylates, sulfonates and quaternary amines [14]. However, unlike neutral oligoethylene glycol groups, these groups are charged and could interfere with potential pH-driven switching studies. We therefore set out to synthesize (Fig. 3) and study triethylene-glycol (TEG) substituted crankshaft terphenyl-dilactone (**15**). We concurrently performed the synthesis of analogous compounds with shorter mono and diethylene glycol solubilizing units. The shorter units did not afford as significant improvements in solubility and potential units longer than TEG were anticipated to result in troublesome purifications due to the highly polar nature of the longer oligoethylene glycol groups. We

found that the TEG groups in **15** to be the perfect compromise in that it solubilized the compound and was also amenable to standard inexpensive purification techniques.

Results and discussion

Crankshaft dilactone **15** with TEG solubilizing groups was synthesized in 10 steps (Fig. 3) from commercial starting materials. 2-Bromo-5-methoxybenzoic acid was isomerized to **10** in two steps in a single pot with a BBr_3 -promoted methyl ether cleavage, followed by a Fischer esterification. Attempts at a more cost-effective methyl ether cleavage on a larger scale using a commonly employed method of heating in HBr and AcOH resulted in bromine migration. Bromine migrations under these conditions are rare, however, aromatic compounds with a bromine atom situated *ortho* to a carboxylic acid group and either *ortho* or *para* to a potential hydroxy substituent are documented to be susceptible [15]. TEG tosylate **8** was synthesized as reported [16] and subsequently substituted onto phenol **10** to achieve TEG-substituted **11**, which was then converted into boronic ester **12** under Miyaura borylation conditions in good yields. Double Suzuki coupling of **12** with

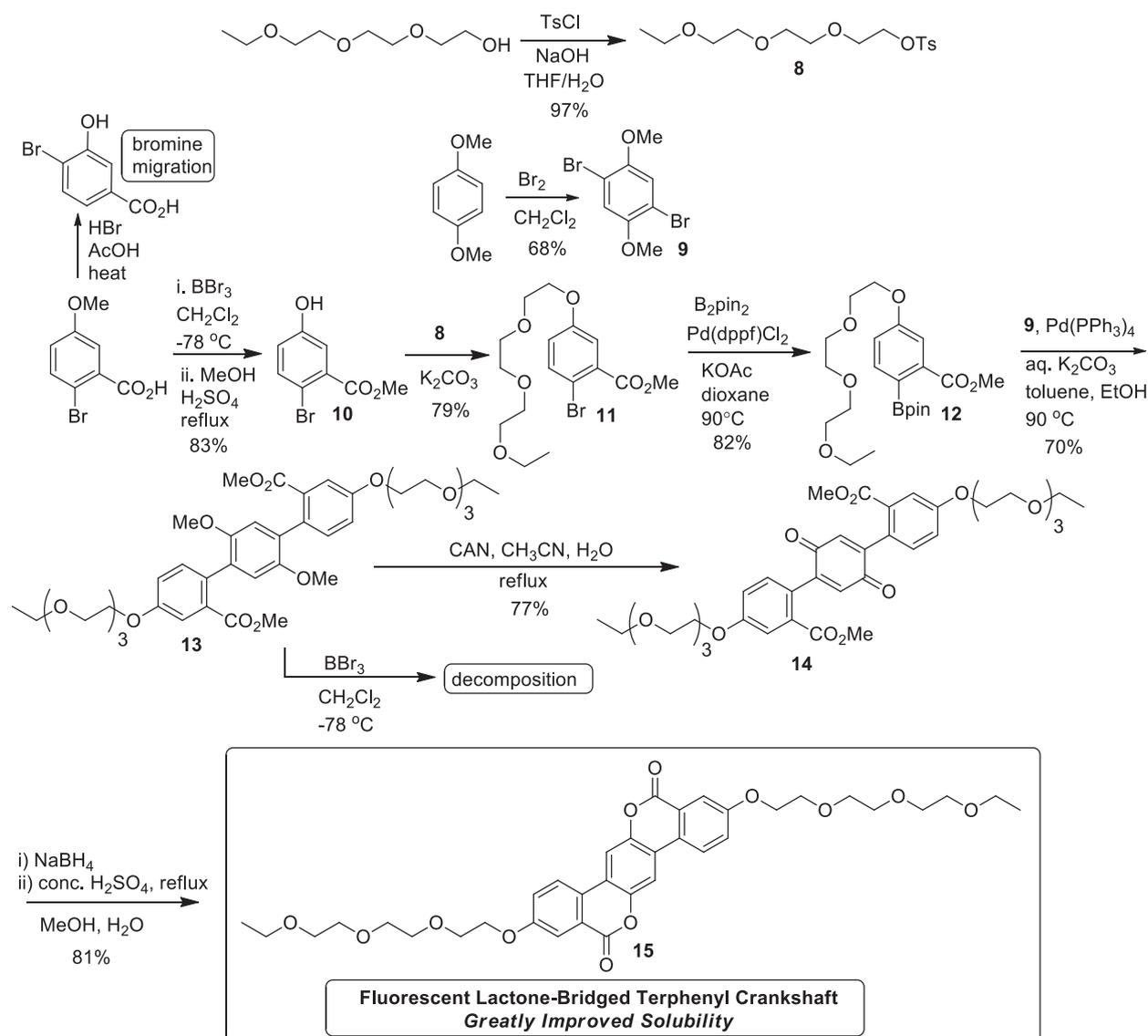


Fig. 3. Synthesis of lactone-bridged terphenyl **15** containing triethylene glycol solubilizing groups.

dibromoarene **9** [9b] resulted in terphenyl **13**. Terphenyl **13**, containing two TEG units, was very challenging to separate from the excess **12** (and its deborylated side product) employed in the Suzuki coupling because of its highly polar nature and strong interactions between the ethylene glycol units of the product and side products. However, after numerous trials, we found that column chromatography with THF in hexane immediately followed by a subsequent column with EtOAc in CH₂Cl₂ was essential to achieve this separation. All other eluent conditions tested resulted in co-elution. In previous studies to achieve crankshafts **2**, **3**, and **5** we found that direct demethylation of terphenyls analogous to **13** with BBr₃ conveniently achieved dilactone-bridged final products in a single step. In this current study, attempts to selectively cleave the methyl ethers on **13** using BBr₃ unfortunately resulted in decomposition, likely due to competing cleavage of the TEG groups, even with careful stoichiometric addition at low temperatures. This necessitated an alternative route consisting of a ceric ammonium nitrate (CAN) oxidative cleavage of the *p*-dimethoxy groups to obtain quinone **14**. Quinone **14** was subsequently reduced with NaBH₄ and then underwent acid-promoted lactonization in a single pot to achieve solid TEG solubilized crankshaft dilactone **15** in good overall yields.

Unlike previously studied lactone-bridged oligophenyls **1–7** (Fig. 2) [9b,9c,11a,11b], TEG-containing **15** displays solubility in a wide variety of solvents (Table 1). Previously reported crankshaft compounds containing the “bridge-flipped” lactone orientation (unsubstituted **4** [11b] and *tert*-butyl solubilized **5** [9b]) show slightly better solubility than isomeric crankshafts **1–3** [9b,11a] or triskelions **6** and **7** [9c]. Compound **1** [11a] has only been shown to dissolve in concentrated H₂SO₄ and compounds **2** [9b], **3** [9b], **6** [9c], and **7** [9c] are sparingly soluble in THF, CH₂Cl₂, CHCl₃, and toluene, often requiring heat to dissolve. The strong π - π intermolecular interactions of crankshafts **1–3** make it difficult to solubilize these compounds, despite **2** and **3** containing *tert*-butyl and 3,5-di-*tert*-butylphenyl solubilizing groups. The strength of their intermolecular interactions can be probed indirectly by simple melting point analysis. Compounds **1** [11a], **2** [9b], and **3** [9b] have very high reported melting points of 420–422 °C, 366 °C, and 440 °C, respectively. Triskelions **6** [9c] and **7** [9c] also display strong intermolecular π - π interactions with melting points in excess of 340 °C. In contrast, TEG-solubilized **15** has a much lower melting point of 160–161 °C, despite having a much greater molar mass than **1** and **2**, and a similar molar mass to **3**. This suggests that the conformational flexibility of the TEG-groups can better overcome π - π interactions and allow for solute-solvent interactions to compete more favorably compared to **1–3**. The higher solubility of **15** makes it more tractable to characterize, process, and potentially more useful in optical applications.

The spectroscopic properties of lactone-bridged terphenyls **2**, **3**, and **5** were studied previously by us (Table 2) [9b]. All three compounds were found to absorb strongly in the near UV to visible region with large molar extinction coefficients (ϵ) all greater than 35,000 M⁻¹cm⁻¹. The restricted rotational motion caused by the lactone bridges between the individual arene units of **2**, **3**, and **5** also resulted in significant visible fluorescence, emitting violet-

Table 2
Electronic absorption and emission data for **2**, **3**, **5**, and **15**.

compd	lowest E abs λ_{max} [nm] (ϵ [M ⁻¹ cm ⁻¹]) ^a	em λ_{max} ^b [nm]	Φ_{F} ^c
2	364 (36832)	385	0.23
3	384 (65080)	394	0.92
5	335 (37983)	439	0.24
15	374 (51400)	405	0.33

^aUV-vis spectral data from **2**, **3**, and **5** dissolved in CH₂Cl₂ and **15** dissolved in CH₃CN. ^bEmission spectral data from **2**, **3**, and **5** dissolved in CH₂Cl₂ and **15** dissolved in CH₃CN and excited at 350 nm. ^cCalculated relative to a quinine sulfate standard dissolved in 0.5 M H₂SO₄ and excited at 350 nm (values corrected for analyte and standard solvents) [21].

blue light with Stokes shifts ranging from 10 to 104 nm and relative Φ_{F} between 0.23 and 0.92. However, these studies were again limited by the poor solubility of these compounds and all spectroscopic studies were required to be done in CH₂Cl₂. Indeed, lactone-bridged terphenyl crankshaft **15** was found to have very favorable optical properties (Table 2), similar to the previously studied **2**, **3**, and **5**. The primary advantage of TEG-solubilized **15** over **2/3/5** is that spectroscopic studies could now be performed in a variety of solvents, but most importantly, a polar solvent. UV-vis studies revealed that **15** had a λ_{max} = 374 nm with very strong molar absorptivity (ϵ = 51400 M⁻¹cm⁻¹) in acetonitrile. Crankshaft **15** also displayed significant blue-violet fluorescence at λ_{max} = 405 nm in acetonitrile with a Φ_{F} = 0.33.

Compounds **2**, **3**, and **5** were originally envisioned as possible pH-driven molecular switches [9b] and TEG-solubilized **15** is also a potential pH-driven switch with switch states similar to those proposed for **2** and **3** (Fig. 4). Unlike simple unsubstituted *p*-terphenyl, the lactone-bridges engineered in terphenyls **2**, **3**, and **15** allows for these compounds to adopt a rigid conformation with restricted rotation, resulting in a high degree of π -orbital overlap between the individual arenes. Although X-ray quality crystals of these compounds were elusive in our hands, evidence of the rigidity of **2**, **3** and **15** can be observed in the significant downfield chemical shifts of the sterically-compressed aromatic H's [17] in the ¹H NMR spectra of these compounds relative to their non-bridged precursors (see previous studies [9b] and supplementary data). This rigidity leads to these compounds being very efficient at absorbing near-UV/visible light and emitting blue-violet light. The potential of **2**, **3**, and **15** as molecular switches lies in the ability of their lactone bridges being readily cleaved by excess tetrabutylammonium hydroxide (TBAOH), which results in non-planar anions **2a**, **3a**, and **15a** with weakened π -overlap. The individual arenes are now no longer rotationally restricted and both absorption and emission of light should be greatly attenuated. The lactone can then be re-formed by addition of trifluoroacetic acid (TFA), and thus the desirable optical properties should return. However, it is known that hydroquinone dianions are highly susceptible to oxidation and, under strongly basic conditions like those required to generate **2a**, **3a**, and **15a**, the resulting benzoquinones could readily decompose [18]. Thus, the switching of these compounds could be limited. In our previous studies [9b] the drastic difference in solubility between **2/3** and **2a/3a** meant that studies probing reversible switching could not be done, since **2a/3a** were found to precipitate upon addition of TBAOH. However, newly synthesized TEG-solubilized **15** can overcome these challenges because both **15** and **15a** should each be at least partially soluble in polar organic solvents.

Since **15** was soluble in acetonitrile, studies could be performed to probe the capabilities of **15** as a molecular switch. We found that the intensity of absorption and emission were drastically reduced when a drop of TBAOH was added to samples of **15** (Fig. 5), suggesting that lactone cleavage was occurring resulting in non-rigid

Table 1
General solubility of **15** in various solvents.

A. Readily dissolves at rt without heating	B. Dissolves with heat and remains in solution after cooling to rt	C. Dissolves with heat but ppt after cooling to rt	D. Insoluble at all T
THF, CH ₂ Cl ₂ , CHCl ₃	dioxane, DMSO, acetone, acetonitrile, EtOAc, DMF, toluene	iPrOH, EtOH, MeOH	Hexane, H ₂ O, diethyl ether

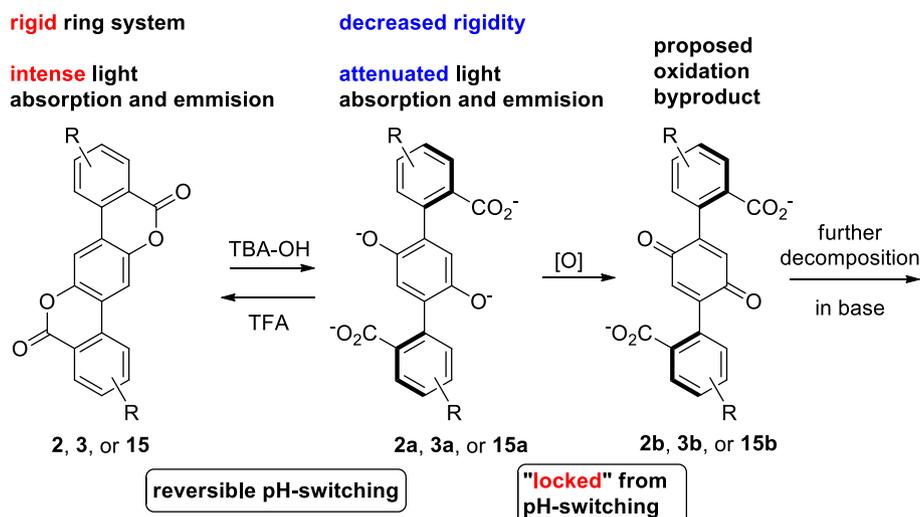


Fig. 4. Proposed pH-driven switching process for **2**, **3** and **15** and possible oxidation and decomposition.

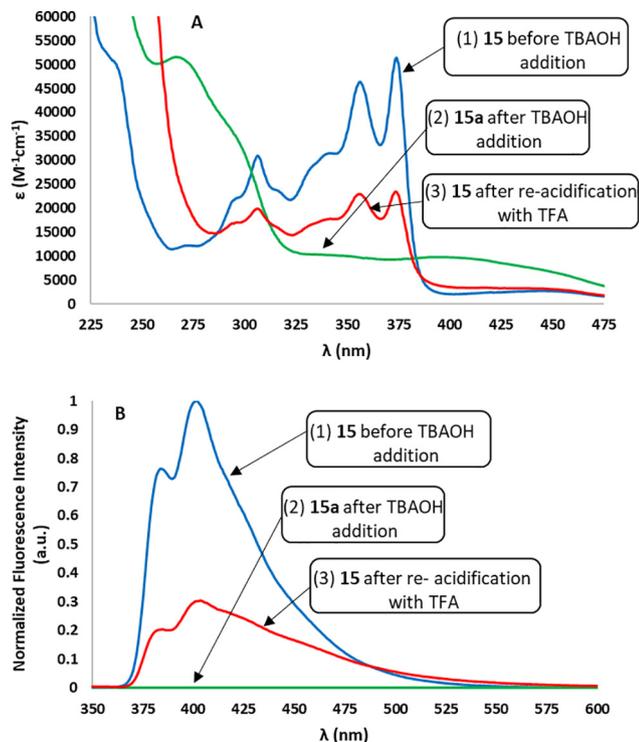


Fig. 5. (A) UV-vis absorption of **15** 1.01×10^{-5} M in CH_3CN (blue), after addition of 1 drop of TBA-OH (green), and after re-acidification with TFA (red). (B) Fluorescence emission scan (excited at 350 nm) of **15** 1.01×10^{-5} M in CH_3CN (blue), after addition of 1 drop of TBA-OH (green), and after re-acidification with TFA (red).

15a. The absorption spectra of **15** is typical of polyaromatics with restricted rotational freedom in that multiple defined peaks are observed due to the multiple vibrational modes of the $\pi \rightarrow \pi^*$ transition, whereas the broad absorption spectra of **15a** is typical of a compound with a higher degree of bond rotational freedom. The identity of **15a** as the product of ring opening was further supported by ^1H NMR studies (see [supplementary data](#)) showing a significant upfield chemical shift of **15a** relative to **15** due to electron donation from the resultant anions as well as a relief from the steric compression of aryl H's induced by adopting a less rigid geometry. Addition of TFA to the ring-opened sample **15a** resulted

in a return to higher absorption and emission, indicating the reforming of **15**, however both absorption and emission were attenuated relative to the original sample of **15** (Fig. 5), indicating some decomposition was occurring during the TBAOH induced ring-opening. Spontaneous oxidation of aryl lactones with characteristics similar to **15** have been reported upon base-promoted lactone cleavage resulting in immediate oxidation to quinone formation [19]; simple 1,4-benzoquinone is known to be sensitive toward strong bases resulting in spontaneous decomposition [18]. These studies enabled by TEG-solubilized **15** establish that terphenyl-dilactone crankshaft shaped compounds like **15** having the potential to be pH-driven molecular switches, albeit with limited switching cycles, or as "turn-off" fluorescent sensors [20] of high pH. Compound **15** was also shown to have striking visible fluorescence in both the solid state and in acetonitrile solution (Fig. 6), emitting bright blue-violet light. The pH-driven switching of **15** could be visibly observed as fluorescence was greatly attenuated upon addition of TBAOH and returned upon addition of TFA.

In summary, TEG-solubilized terphenyl **15** with a crankshaft architecture was synthesized and its optical properties were studied. Lactone-bridged rotationally restricted oligoarenes are a rare and unusual class of molecules with attractive optical properties, and only a few known examples to date. However, they are

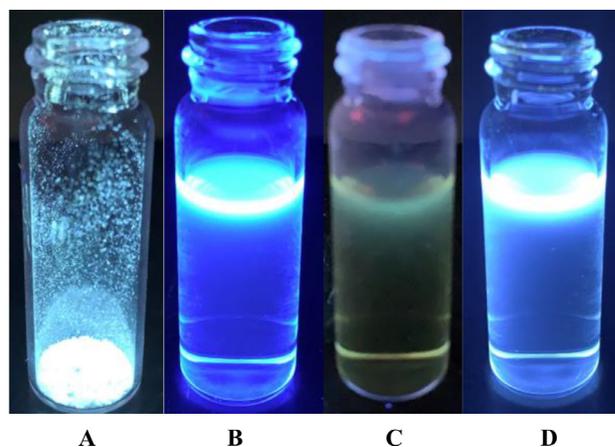


Fig. 6. (A) Solid sample of **15** irradiated by UV light. (B) **15** in CH_3CN (1.0×10^{-3} M) irradiated by UV light. (C) Sample from (B) after addition of 1 drop of TBA-OH. (D) Sample from (C) after re-acidification with TFA.

plagued by poor solubility, even when appended with commonly utilized alkyl and aryl solubilizing groups which would limit their processability. The much-improved solubility of **15** in a wide variety of solvents compared to previously studied analogs has allowed for detailed optical studies and has enhanced its potential for applications. Crankshaft **15** was found to have highly desirable optical properties, strongly absorbing in the near-UV/visible and emitting bright blue-violet light in both the solid state and in solution. The improved solubility of **15** has also enabled detailed studies of its, and by extension previously studied analogs, potential for pH-driven conformational switching. It was discovered that **15** is capable of limited conformational switching via ring-opening in base and ring-closing in acid. The base-promoted ring-opening of **15** resulted in severe attenuation of light absorption and emission and the subsequent acid-promoted ring-closing resulted in a return to the previous state, although weakened relative to the initial sample. The ring-opened state **15a** was found to be only semi-stable, likely through oxidative decomposition, and thus iterative switching is restricted by this factor. However, **15** has been shown to be, at minimum, a “turn-off” fluorescent sensor at high pH. From the switching studies enabled by **15** we propose to explore the possibility of a lactone “bridge-flipped” analog of **15** (e.g. TEG-solubilized **5**) which should be less sensitive to oxidative degradation and might function better as a pH-driven switch. TEG-solubilized **15** has been shown to be much more tractable than previous studied crankshaft dilactones while maintaining desirable optical properties. Applying TEG solubilizing groups to lactone bridged oligophenylenes as a general synthetic strategy should result in facile processing for potential optical devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tetlet.2020.152429>.

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