Sugar–Poly(*para*-phenylene ethynylene) Conjugates as Sensory Materials: Efficient Quenching by Hg²⁺ and Pb²⁺ Ions

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Abstract: Three polar poly(*para*-phenylene ethynylene)s (PPE) were synthesized by utilizing the Heck–Sonogashira protocol. Two of the PPEs carry β-glucopyranose substituents. Depending upon the linker used between the glycol units and the backbone, the fluorescence of these PPEs can be quenched by Hg²⁺ and Pb²⁺ to a varying degree. Monomeric model compounds that are substituted with only one glucose unit are not efficiently quenched. The presence of many glucose substituents in one PPE assembly led to a large increase in the binding constant to Hg²⁺ and quenching of the fluorescence was amplified.

Keywords: alkynes · conjugated polymers · glucose · sensors · transition metals

Introduction

Herein we report the surprisingly efficient fluorescence quenching of sugar-substituted poly(*para*-phenylene ethynylene)s (PPE) **2** and **3** by Hg²⁺ and Pb²⁺ ions. Lead and mercury are heavy metals that play a large role in environmental politics due to their high general and specific neurotoxicity.[1] Adverse long-term health effects are significant even upon exposure to trace concentrations of these elements. Mercury and lead are prevalent as environmental pollutants generated by industrial processes including the large-scale combustion of coal (mercury) and the long-standing environmental pollution by lead paint (now banned).[2] As a consequence, the detection and determination of lead and mercury is of great scientific, medical, and economic interest. The classic approaches to lead and mercury sensing are atomic absorption spectrometry, inductively coupled plasma mass spectrometry, anodic stripping voltammetry, and X-ray fluorescence spectrometry, all of which require expensive hardware, sophisticated sample treatment, and well-trained operators.[3] As a consequence, the development of sensitive "dip-stick" tests for mercury and lead ions is attractive. Progress has been made, however, with recently reported Pb²⁺ or Hg²⁺ sensors that utilize either specific DNA and peptides or small fluorescent dyes, such as hydroxyquinoline-substituted crown ethers.[4–7]

Conjugated polymers are organic semiconductors. They find widespread use in electro-optical devices as well as in analytical detection schemes.[8–10] The highly fluorescent PPEs[11,12] have been exploited as sensory materials for electron-poor aromatics,[13] fluoride ions,[14] streptavidin,[15] and some metal cations.[16] As an important note, a subtle difference in analyte can greatly affect the sensing action of conjugated polymers, and in some cases, closely related analytes can be discerned with surprising efficiency. The reason for the often observed selectivity is not clear but can be exploited to detect a specific analyte, an example being Tour's iodide sensor.[17]

The interaction of saccharides with heavy metals has been only sparingly investigated, despite the importance of cellulose copper complexes that allow for the processing of cuprammonium rayon.[18] Few reports describe the interaction of monomeric sugars with mercury or lead ions. It was claimed that simple sugars form chelate complexes of unknown structure that show stability constants of ≈10⁵ at high ionic strengths in water.[19a] A second study contended that "there is no major interaction between D-glucose and the zinc-group metals (Zn, Cd, Hg) in aqueous solution".[19b] A third study[19c] investigated the coordination of mercury salts to sugar amino acids. The authors of this study conclude from their data that complex formation is dependent upon the chosen counterion for the mercury salt. A cited example was HgCl₂, dissolving mostly undissociated into water. The solid-state structure of Hg²⁺ and Pb²⁺ complexes of sugars are largely unknown and only recently Klüfers et al.[20] have obtained crystal structures of some sugar–transition-metal complexes. An instructive case is the reaction of γ-cyclodextrin with Pb(NO₃)₂ which led to a sixteen-fold plumbated cyclodextrin torus (solid state). Not all sugars

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form crystalline complexes with lead ions. According to Klüfers et al.,[20] such complexes appear gelatinous, detracting attention from biologically and medicinally interesting sugar–transition-metal coordination. And while the unspecific interaction of some polythiophene derivatives with lead and mercury salts at high concentrations has been studied by McCullough et al.,[21] the chromic response was attributed to the conformational change of the conjugated backbone. Herein, we report the synthesis of PPEs 1–3 and their sensitive but differential fluorescence quenching by Hg^{2+} and Pb^{2+} ions.

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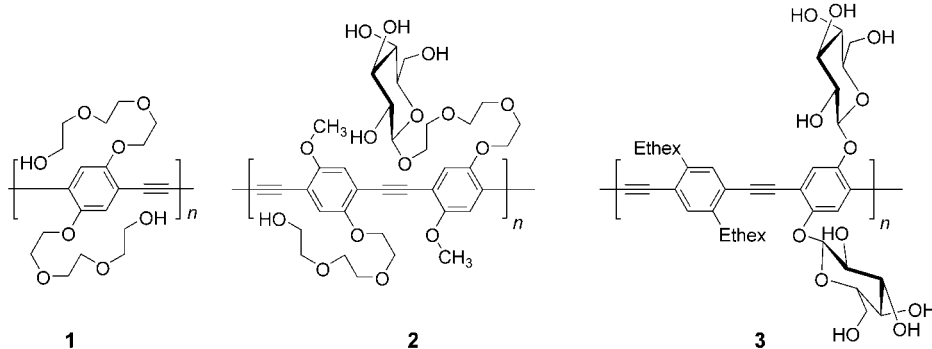
Results

Synthesis: Polymers 1 and 2 and the model compounds 7b and 11b were synthesized according to Schemes 1 and 2, re-
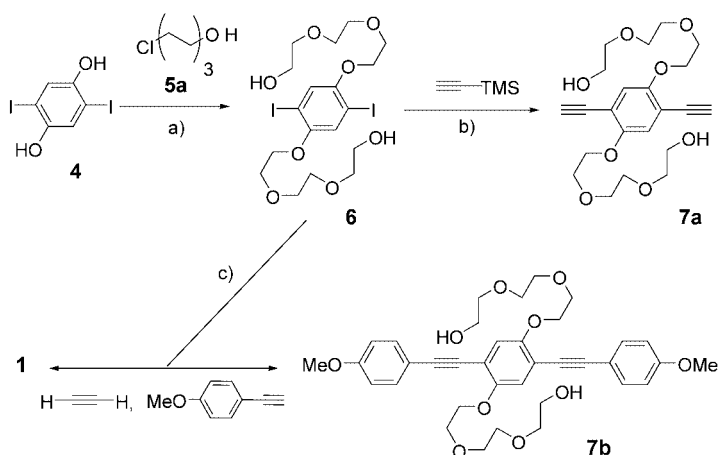
Scheme 1. Synthesis of the polymer 1 and the model compound 7b. a) K_2CO_3, DMF; b) [PdCl$_2$(PPh$_3$)$_2$], CuI/THF, piperidine, then Bu$_4$NF; c) [PdCl$_2$(PPh$_3$)$_2$], CuI/THF, piperidine.

spectively, while polymer 3 was prepared according to ref. [22a] (Ethex: 1,4-diethynyl-2,5-bis(ethylhexyl)benzene). Starting from diiodohydroquinone (4), etherification with the polar chloride 5a furnished diiodide 6 (34%) (Scheme 1). Polymerization utilizing the acetylene gas method[22b] produced polymer 1 in excellent yield (85%) with a number-average molecular weight (M_n) of 9.5×10^3 amu and a polydispersity (M_w/M_n) of 1.85. Another monomer, 7a, was obtained in a 31% yield by the Pd-catalyzed alkynylation of 6 with (trimethylsilyl)acetylene followed by removal

of the TMS groups by tetrabutylammonium fluoride. To access the model compound 7b, diiodide 6 was coupled to 4-methoxyphenylacetylene under standard Pd-catalyzed coupling conditions.[11,23] The trimer 7b was obtained analytically pure in a 54% yield after precipitation and washing with a mixture of ethyl acetate/hexanes (EtOAc/Hex, 1:3).

The glucose-substituted polymer 2 and its model compound 11b were obtained in an analogous way. Starting from 2,5-diiodo-4-methoxyphenol (8), attachment of the triethylene glycol unit using iodide 5b and K_2CO_3 produced 9. A Pd-catalyzed reaction with (trimethylsilyl)acetylene led to monomer 10, while glycosylation of 9 using glucose penta-acetate in the presence of BF$_3$·OEt$_2$ in dichloromethane[24] gave rise to the clean formation of 11a in a 76% yield. Only the β-anomer was observed under these conditions, analogous to the literature.[24] If diiodide 11a is coupled to 10 by using standard Heck–Cassar–Sonogashira[23] conditions, deacetylated polymer 2 is formed in a 93% yield with an M_n of 35×10^3 amu and an M_w/M_n of 1.52. Coupling of 11a to 4-methoxyphenylacetylene under the same conditions gave the analytically pure, deacetylated model compound 11b (63% yield) after precipitation and washing with a mixture of EtOAc/Hex (1:3). The polymers and the model compounds are sparingly soluble in water, but dissolve well in aprotic polar solvents such as DMSO or dimethylformamide (DMF) forming clear blue/green fluorescent solutions. The concomitant deacetylation of glucose when preparing 2 and 11b is gratifying and occurs as a result of the action of the nucleophilic piperidine. Varying amounts of N-acetylpiperidine are formed as byproduct. The in situ deprotection is a convenient and mild way of removing the acetyl groups cleanly.

Optical properties of the polymers and their model compounds: PPEs 1 and 2 and their model compounds exhibit the expected optical behavior.[11] In solution, the optical properties of 1 and 2 are only determined by the dialkoxy–PPE backbone and are not influenced by the presence of the glucose or oligo(ethylene glycol) side chains. In Figure 1, absorption and emission spectra of polymer 2 and model compound 11b are shown. The optical properties of 2 in DMF are identical, within experimental error, to those reported by other groups ($\lambda_{max}^{abs} = 410$–452 nm, $\lambda_{max}^{em} = 455$–476 nm) for alkoxy–PPEs.[11] The quantum yield (Φ) of 2 in DMF is 0.63, while that of 11b in DMF is 0.76. The quantum yields for 1 and 7b are similar, as are their spectral features.

Sensing of lead and mercury—comparison of polymers to model compounds

Polymers: Polymers 2 and 3 were originally designed to test the binding of PPEs to lectins, that is, sugar binding proteins. In binding studies with the lectin concanavalin A
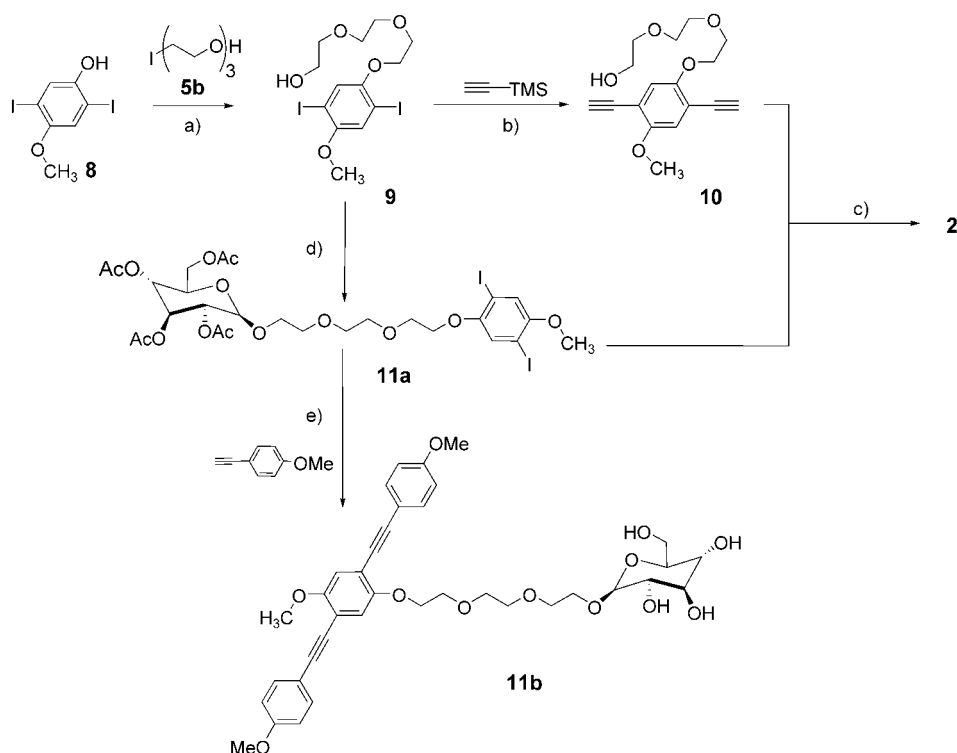
Scheme 2. Synthesis of the model compound **11b** and the polymer **2**. a) K_2CO_3, acetone; b) [PdCl$_2$(PPh$_3$)$_2$], CuI/THF, piperidine, then Bu$_4$NF; c) [PdCl$_2$(PPh$_3$)$_2$], CuI/THF, piperidine; d) glucose(OAc)$_5$, BF$_3$·OEt$_2$; e) [PdCl$_2$(PPh$_3$)$_2$], CuI/THF, piperidine, then Bu$_4$NF.
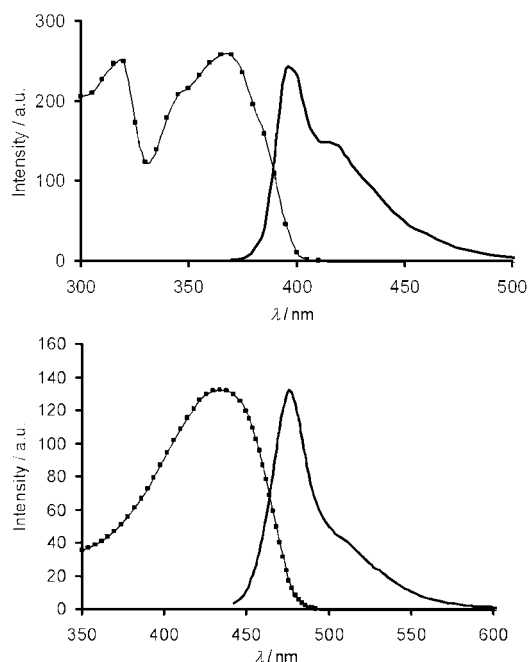

Figure 1. Absorption (■) and emission (——) spectra (a.u. = arbitrary units) of model compound **11b** in DMF (top; $\lambda_{max}^{abs}=369$ nm, $\lambda_{max}^{em}=397$ nm) and glucose–PPE **2** in DMF (bottom; $\lambda_{max}^{abs}=436$ nm, $\lambda_{max}^{em}=476$ nm).

(Con A), we found that upon addition of the lectin-cofactor Mn^{2+} to the solution of glucose–PPE **2** and Con A, a small but significant quenching of the fluorescence of **2** occurred.

The quenching of polymers **2** and **3** with other transition-metal ions was investigated. Most transition-metal ions did not elicit any response, however Pb^{2+} and Hg^{2+} did (Table 1).

In our first experiment we exposed **2** to HgCl$_2$ and found that significant quenching of **2** occurred with a K_{SV} of 11×10^3. Polymers **1** and **3**, however, were not quenched by mercury chloride. Mercury chloride is largely undissociated in water, and probably even less dissociated in DMF. In a second set of experiments we exposed **1–3** to mercury nitrate, which is more ionic. Here the K_{SV} value increased to 38×10^3 for **2** and a moderate K_{SV} value of 2.9×10^3 for the non-glycosylated polymer **1** was observed. Polymer **3** was not quenched at all by Hg(NO$_3$)$_2$. Is the nature of the counterion or the dissociation constant of importance for the fluorescence quenching of the polymers? We chose mercury acetate and mercury trifluoroacetate (tfa) as additional quenchers, the acetate having a low dissociation constant in DMF, while mercury trifluoroacetate is more dissociated. Mercury chloride and mercury acetate are grouped as low-dissociating salts, while mercury nitrate and mercury trifluoroacetate show a considerably higher concentration of free mercury ions. The quenching of **1–3** with mercury acetate is similar to that observed for quenching with HgCl$_2$, and the results of the quenching experiments of **1–3** with mercuric trifluoroacetate ([Hg(tfa)$_2$]) resemble those obtained for the nitrate, with [Hg(tfa)$_2$] being a somewhat better quencher than the nitrate. Glucose–PPE **2** is quenched by mercury trifluoroacetate effectively ($K_{SV}=48\times10^3$) while the oligo(ethylene glycol)-substituted PPE (**1**) shows a quenching of 2.9×10^3 and polymer **3** is quenched only weakly by mercury trifluoroacetate. To test the quenching of these PPEs by an unspecific quencher we investigated the effect of the addition of 4-nitrophenol to **1–3**. The obtained K_{SV} values are considerably lower than those for the mercury salts and all similar, in the range of $1–2\times10^3$. The data suggest that the chemical nature of the counterion to the Hg^{2+} ion does not play a significant role in the interaction of the PPEs with the transition-metal ion, only the dissociation seems to be important. Addition of sodium acetate does not quench the fluorescence of polymers **1–3**, further reinforcing the trend of the chemical insignificance of the chemical nature of the counterion.

The quenching effect of lead was investigated. PPEs **1–3** show significant K_{SV} values. Polymer **3** showed the largest value with $K_{SV}=72\times10^3$. Only lead acetate quenches the

Table 1. The degree of quenching observed with Hg^{2+} and Pb^{2+} ions, in addition to some other quenchers, by polymers **1–3** and model compound trimers **7b** and **11b** in DMF.

	1 K_{SV}	**7b** K_{SV}	K_{SV}^1/K_{SV}^{7b}	**2** K_{SV}	**11b** K_{SV}	K_{SV}^2/K_{SV}^{11b}	**3** K_{SV}
$HgCl_2$	NQ[a]	NQ	–	11×10^3	NQ	>1000	NQ
$Hg(OAc)_2$	NQ	NQ	–	16×10^3	NQ	>1000	<10
$Hg(NO_3)_2$	2.9×10^3	520	5.6	38×10^3	1.1×10^3	35	NQ
$[Hg(tfa)_2]$[b]	2.9×10^3	200	15	48×10^3	0.91×10^3	53	<10
$Pb(OAc)_2$	15×10^3	NQ	>1000	25×10^3	<10	>250	72×10^3
$Pb(NO_3)_2$	<10	NQ	–	<10	<10	–	<10
NaOAc	NQ	nd[c]	–	<10	nd[c]	–	NQ
4-nitrophenol	1.2×10^3	nd[c]	–	1.3×10^3	nd[c]	–	2.1×10^3
paraquat dichloride	520	130	4	260	290	1	4.5×10^3

[a] NQ = no quenching observed. [b] tfa: trifluoroacetate. [c] nd = not determined.

polymers; the nitrate has an almost negligible effect upon the fluorescence of the polymers. The presence of the acetate ion seems to be an auxiliary in the coordination of the lead ions to the sugar-coated PPEs, but quenching is not a function of the acetate anion as such.

Model compounds: To investigate if the binding of the transition metals to the sugar-coated PPEs is cooperative[25] or if the molecular-wire effect as investigated by Swager for a PPE model system[26] plays a role, the model compounds' (**7b**, **11b**) quenching behavior towards mercury and lead salts was investigated. Neither **7b** nor **11b** were quenched when mercury chloride or mercury acetate were added to them in DMF (Table 1). In the case of $Hg(NO_3)_2$ and $[Hg(tfa)_2]$, both **7b** and **11b** were quenched modestly (Table 1) with K_{SV} values in the range of $0.2–1.1 \times 10^3$.

Quenching polymers and model compounds with 4-nitrophenol and paraquat (1,1'-dimethyl-4,4'-bipyridinium) dichloride: To obtain a standard for the sensing abilities of the model compounds and the polymers, a reliable nonbinding quencher was investigated. Using 4-nitrophenol, K_{SV} values between $1–2 \times 10^3$ for polymers **1–3** were obtained. For the model compounds, nitrophenol was not a viable quencher as its absorption wavelength overlaps with the emission wavelength of **7b** and **11b**. Instead, paraquat dichloride was a chosen as the quencher. An alkoxy–PPE was quenched by paraquat with a K_{SV} value of $5–6 \times 10^2$.[26] We find similar values for **1** ($K_{SV} = 520$) and **2** ($K_{SV} = 260$). The model compounds **7b** and **11b** showed K_{SV} values of 130 and 290, respectively. However, polymer **3** displayed much more efficient quenching ($K_{SV} = 4.5 \times 10^3$) suggesting a ground-state complex of **3** with paraquat dichloride.

Discussion

The literature claims that sugars form complexes that bind tightly to Hg^{2+} in solution. We have made monomeric (**7b**, **11**) and polymeric (**2**, **3**) glucose derivatives of arylene ethynylenes. All of the phenylene ethynylenes are highly fluorescent and are attached to the glucose residue through the

anomeric carbon. Mercury is a heavy-metal ion and will quench fluorescence of a dye by enhanced spin–orbit coupling when in close proximity. As a quantitative measure of quenching, the Stern–Volmer equation [Eq. (1)] is a useful tool. The quencher concentration is [Q], K_{SV} is the Stern–Volmer constant, F_0 is the fluorescence intensity measured without additional quencher, and $F_{[Q]}$ is the fluorescence intensity with quencher at a given [Q].[27]

$$(F_0/F_{[Q]}) = 1 + K_{SV}[Q] \quad \text{or} \quad K_{SV} = \{(F_0/F) - 1\}/[Q] \qquad (1)$$

The slope of the graph ($F_0/F_{[Q]}$) versus [Q] equals K_{SV}. The more sensitive a given system is to a specific quencher, the steeper the Stern–Volmer plot and the higher the K_{SV} value. Quenching processes can be generalized as having two mechanisms, namely, they can be static or dynamic in nature.[27] In static quenching, the fluorophore and the quencher form a complex in the ground state. Upon irradiation, quenching of the excited fluorophore by the complexed quencher occurs. In dynamic or collision quenching, the excited state of the fluorophore is quenched by collision with the quencher. If either one of these mechanisms is predominant in a given system, a linear Stern–Volmer relationship occurs. A linear relationship is observed in the herein investigated Stern–Volmer plots of the quenching of the PPEs **1–3**, as shown in Figure 2 for glucose–PPE **2**. Un-aggregated PPEs in solutions show a short fluorescence lifetime (around 0.3–0.5 ns),[11] and their fluorescence lifetimes do not change upon addition of quencher.[26] It can be assumed that static quenching is the prevalent mechanism operating in the cases investigated here.[26] In the case of static quenching, the Stern–Volmer constant is equal to the binding con-
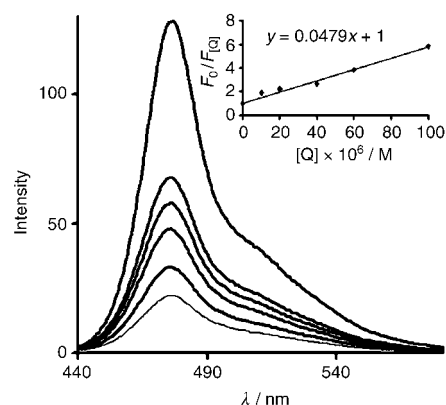

Figure 2. Spectra showing the fluorescence emitted during the quenching of glucose–PPE **2** by $[Hg(tfa)_2]$ in DMF: quencher concentrations (M) from the bottom upwards are 1×10^{-4}, 6×10^{-5}, 4×10^{-5}, 2×10^{-5}, and 1×10^{-5}; the top spectrum is without quencher. The inset shows the Stern–Volmer plot. The extracted Stern–Volmer constant is $K_{SV} = 48 \times 10^3$.

stant of the quencher to the fluorophore;[28] K_{SV} conveniently delivers the binding constant of mercury and lead salts to sugar derivatives.

Mercury: We observed linear Stern–Volmer plots and in some cases large K_{SV} values using mercury salts as quenchers. Quenching is most efficient if a sugar unit is present (**2**) but a triethylene glycol linker also seems necessary. Polymers **1** and **3** are lacking either one of these features. If only the ethylene glycol group is present (**1**) quenching is observed for dissociated mercury salts, but no quenching is recorded for the less-dissociated acetate and chloride. However, polymer **2** is quenched by all of the tested mercury salts. The model compounds **7b** and **11b** do not show any quenching with mercury chloride or acetate. However, in the case of the trifluoroacetate and the nitrate, moderately efficient quenching is observed (Figure 3). According to Table 1, the
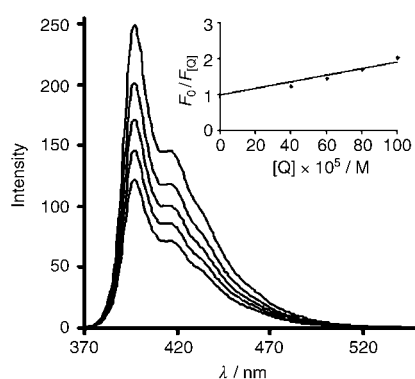

Figure 3. Spectra showing the fluorescence emitted during the quenching of model compound **11b** by [Hg(tfa)$_2$] in DMF: quencher concentrations (M) from the bottom upwards are 1×10^{-3}, 8×10^{-4}, 6×10^{-4}, and 4×10^{-4}; the top spectrum is without quencher. The inset shows the Stern–Volmer plot. The extracted Stern–Volmer constant is $K_{SV} = 0.9 \times 10^3$.

binding of the model compounds to Hg^{2+} range from $K_{SV} = 200$–1100; **7b** and **11b** bind better to Hg(NO$_3$)$_2$ than to [Hg(tfa)$_2$].

The largest increases of quenching ability are found when comparing the quenching of **11b** with mercury acetate or mercury chloride with the quenching of **2** to the same salts. The increase of the binding constant values via K_{SV} is larger than 10^3. In the case of the nitrate and the trifluoroacetate, the increase when going from model compound to polymer is significantly smaller but still a factor of 35–53. When comparing **7b** to **1**, the increase in K_{SV} is less pronounced ($K_{SV}^{1}/K_{SV}^{7b} = 6$–15).

When comparing the model compound and polymer we have two independent effects that enhance quenching. The first one is the molecular-wire effect, as described by Swager.[26] In this scenario, amplified quenching is achieved by the connection of the sensory elements to the conjugated backbone. Complexing one quencher will therefore shut down the fluorescence of the whole chain. Reported enhancements in K_{SV} range from 17 for a nonfunctionalized PPE versus a nonfunctionalized PE-trimer to a 60-fold en-

hancement in a specifically designed model/PPE system. The 60-fold enhancement was the largest reported and might represent the upper limit for the molecular-wire effect in solution.[26]

In one group we see enhancements of quenching that range from factors of 6 to 35. In a second group of experiments we observed **2** to be quenched with Hg^{2+} salts by a factor >1000 times better than model **11b**. The enhanced quenching can not be due only to the molecular-wire effect, cooperative binding must also be present. In cooperative binding (Figure 4),[25] two or more sugar substituents of one
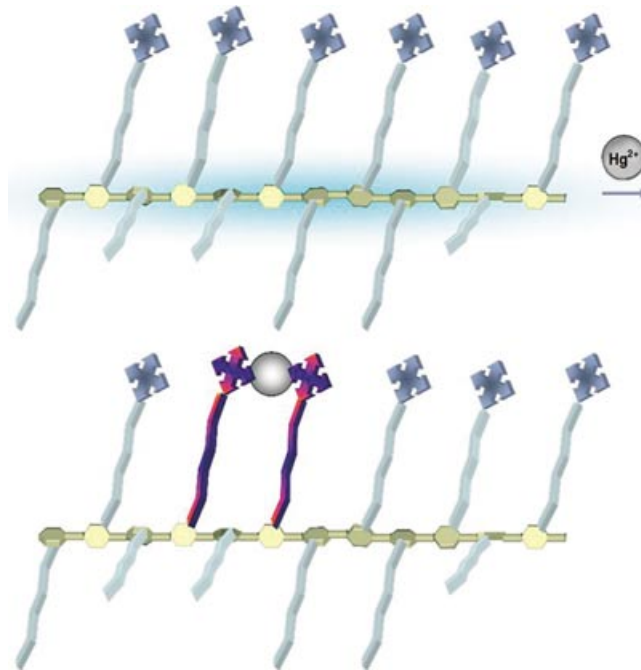

Figure 4. Schematic representation of the cooperative quenching of glucose–PPE **2** by mercury trifluoroacetate. Two or more sugar substituents (crossed arrows) of one chain partake in the complexation of a single mercury ion (sphere).

chain partake in the complexation of a single mercury ion or HgX$_2$-molecule to give a significantly higher K_{SV} value for **2** than for **11b** thus explaining the differences in quenching of **2** versus **11b** with mercury acetate or mercury chloride.

The polymers' (**1–3**) fluorescence is efficiently quenched by lead acetate, with a K_{SV} range of 15–72×10^3. Lead nitrate does not quench the polymers' fluorescence at all. The largest K_{SV} value resulted when **3** was quenched by lead acetate, but model compounds did not show any quenching. We can speculate that **1–3** form a complex with lead ions in which the acetate groups might act as (a) supporting and/or bridging ligand(s) and increase binding. The quenching enhancement shown by lead acetate is large for **1–3** suggesting that both the molecular-wire effect and cooperative binding are important, that is, two or more sugar substituents are involved in the binding event.[27] We suspect that the unusually high acidities of Hg^{2+} and Pb^{2+}[29] led to a higher than expected binding constant to alcohol functionalities. With the

enhanced acidity of the OH groups in sugars (pK_a = 12.3–12.4)[30] this binding should be somewhat more enhanced. We can speculate that a hexacoordinated Hg^{2+} ion surrounded by three glucose molecules, of which two are mono-deprotonated, is involved in these complexes (Figure 5). In this case, the *trans*-arranged 4- and 5- hydroxyl
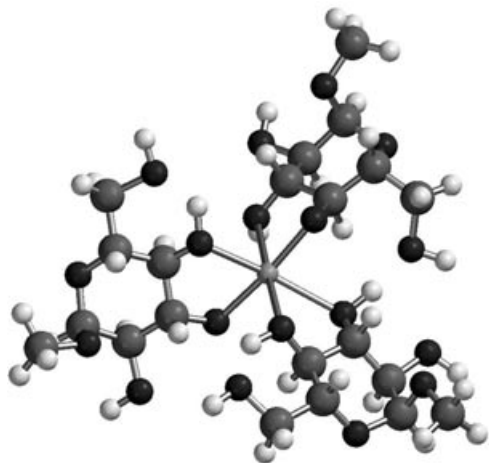

Figure 5. Speculative molecular model of a [Hg(glucose)$_3$] complex. Note that two of the three sugar moieties are deprotonated for charge neutralization.

groups could operate in a chelating fashion. Alternatively the 6-CH$_2$OH groups and the 5-hydroxyl group of the glucose substituent could be involved in a trimeric heavy-metal chelate.

Conclusion

In summary, novel and polar PPEs **1** and **2** were made by using the Pd-catalyzed coupling reaction of the Heck–Cassar–Sonogashira–Hagihara type.[11] Fluorescence quenching of PPE **2** and its monomeric model compound **11b** with mercury and lead salts was investigated. For both metals we found dramatic enhancements of the quenching when going from **11b** to the sugar-coated PPE **2**. In some cases the enhancements are too large to be explained by the molecular-wire effect alone. In these cases a cooperative binding effect between two or more neighboring glucose units placed along the conjugated backbone must play a significant role in the quenching experiments. However, the large complexation constants for mercury ions with monomeric sugars reported in the literature[18] are not borne out by our investigation. In future experiments we will make PPEs that contain additional auxiliary metal-sensing entities, such as thiol and/or aza crown functionalities in addition to the sugar substituents.

It is of importance that sugar-substituted polymers are capable of detecting mercury and lead salts with quite high sensitivity, particularly because hydroxyl groups are not the classic ligands for soft metals.

Experimental Section

Synthesis of 2,5-diiodo-4-methoxyphenol (8): 1,4-Dimethoxy-2,5-diiodo-benzene (9.28 g, 23.8 mmol) was dissolved in dichloromethane (300 mL). The reaction flask was cooled to −78 °C in a dry ice/acetone bath. An 1 M solution of boron tribromide (23.8 mL, 23.8 mmol) in CH$_2$Cl$_2$ was slowly added through the condenser. The reaction mixture was stirred under nitrogen at room temperature for 16 h. Then water (200 mL) was added to the flask. The organic layers were dried over MgSO$_4$ and evaporated to dryness. The product was purified by column chromatography (ethyl acetate/hexanes 1:2). The solid was obtained in a 68% yield (6.80 g). M.p. 115–116 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37 (s, 1H; Ar−H), 7.00 (s, 1H; Ar−H), 5.01 (s, 1H; Ar−H), 3.78 ppm (s, 3H; C−H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 152.96, 149.88, 124.98, 119.67, 86.74, 84.50, 57.22 ppm; IR (KBr): $\tilde{\nu}$ = 3258, 2043, 1487, 1393, 1199, 1056, 1024, 854, 770 cm^{-1}; elemental analysis calcd (%) for C$_7$H$_6$I$_2$O$_2$: C 22.36, H 1.61; found: C 22.24, H 1.66.

Synthesis of 9: Compound **8** (3.01 g, 8.00 mmol) and 2-[2-(2-iodoethoxy)ethoxy]ethanol (2.50 g, 9.60 mmol) were dissolved in acetone (30 mL). Potassium carbonate (11.0 g, 80.0 mmol) was added to the solution. The reaction mixture was stirred under nitrogen at the reflux temperature for 48 h. After the solution was cooled, the solid was filtered off and washed with acetone. The solvent was evaporated and the reaction mixture was extracted three times with chloroform. The organic layers were dried over MgSO$_4$ and evaporated to dryness. The product was purified by column chromatography (ethyl acetate/hexanes 1:1). A colorless solid was obtained (3.10 g, 76%). M.p. 55–56 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.23 (s, 1H; Ar−H), 7.15 (s, 1H; Ar−H), 4.08 (t, J(H,H) = 4.6 Hz, 2H; C−H), 3.86 (t, J(H,H) = 4.6 Hz, 2H; C−H,), 3.79 (s, 3H; C−H), 3.77 (t, J(H,H) = 4.4 Hz, 2H; C−H), 3.71 (t, J(H,H) = 4.6 Hz, 2H; C−H), 3.68 (t, J(H,H) = 4.6 Hz, 2H; C−H), 3.60 ppm (t, J(H,H) = 4.55 Hz, 2H; C−H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 153.41, 152.55, 123.63, 121.17, 86.46, 85.32, 72.46, 71.14, 70.48, 70.29, 69.59, 61.78, 57.11 ppm; IR (KBr): $\tilde{\nu}$ = 3421, 2887, 1486, 1435, 1352, 1216, 1124, 1062, 1022, 854, 777 cm^{-1}; elemental analysis calcd (%) for C$_{13}$H$_{18}$I$_2$O$_5$: C 30.73, H 3.57; found: C 30.86, H 3.59.

Synthesis of 10: Compound **9** (1.02 g, 2.00 mmol) and (trimethylsilyl)-ethyne (0.7 mL, 5.0 mmol) were reacted in diisopropylamine/THF (1:4 v/v; 20 mL) in the presence of CuI (4 mg, 0.02 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (14 mg, 0.02 mmol). The solution was stirred overnight at room temperature. The mixture was filtered to remove the ammonium salts and the solvent mixture was removed in vacuo. The solid residue was dissolved in THF and a solution of tetrabutylammonium fluoride (1 M) in THF was added. The reaction mixture was stirred for 10 min at room temperature and the solvent was removed in vacuo. The product was isolated after chromatography on a silica-gel column (ethyl acetate/hexanes/MeOH 20:20:1) as a pale-yellow solid (275 mg, 45%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.10 (s, 1H; Ar−H), 7.06 (s, 1H; Ar−H), 4.57 (t, J(H,H) = 5.50 Hz, 1H; O−H), 4.39 (d, J(H,H) = 5.15 Hz, 2H; C−H), 4.11 (t, J(H,H) = 4.75 Hz, 2H; O−C−H), 3.78 (s, 3H; O−C−H), 3.73 (t, J(H,H) = 4.55 Hz, 2H; O−C−H), 3.62 (t, J(H,H) = 4.3 Hz, 2H; O−C−H), 3.54 (t, J(H,H) = 4.3 Hz, 2H; O−C−H), 3.50 (t, J(H,H) = 5.25 Hz, 2H; O−C−H), 3.43 ppm (t, J(H,H) = 5.15 Hz, 2H; O−C−H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 154.33, 153.37, 118.24, 115.64, 113.32, 112.32, 82.85, 82.77, 79.49, 79.37, 72.38, 70.89, 70.27, 69.42, 69.32, 61.56, 56.21 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3276, 2869, 1630, 1499, 1456, 1393, 1276, 1221, 1055, 1014, 864 cm^{-1}; elemental analysis calcd (%) for C$_{17}$H$_{20}$O$_5$: C 67.09, H 6.62; found: C 66.00, H 7.14.

Synthesis of 11a: β-Glucosepentaacetate (1.52 g, 3.00 mmol) and diiodide **9** (1.17 g, 3.00 mmol) were dissolved in anhydrous CH$_2$Cl$_2$ (10 mL), then BF$_3$·OEt$_2$ (0.3 mL, 2.4 mmol) was added slowly. The reaction mixture was stirred at room temperature for 24 h and then poured into 5% aqueous NaHCO$_3$ (20 mL). The organic layer was separated, washed with 5% aqueous NaHCO$_3$ and water. The organic phase was dried over MgSO$_4$ and evaporated to dryness. The product was isolated by column chromatography (ethyl acetate/hexanes/methanol 20:20:1). The product was obtained as oil (1.24 g, 76%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.15 (s, 1H; Ar−H), 7.07 (s, 1H; Ar−H), 5.07 (t, J(H,H) = 9.5 Hz, 1H; C−H), 4.96 (t, J(H,H) = 9.7 Hz, 1H; C−H), 4.87 (t, J(H,H) = 9.6 Hz, 1H; C−H), 4.51 (d, J(H,H) = 8.0 Hz, 1H; C−H), 4.14 (q, 1H; C−H), 4.00 (m, 3H; C−H), 3.83

(m, 1H; C–H), 3.76 (t, J(H,H) = 4.95 Hz, 2H; C–H,), 3.71 (s, 3H; C–H), 3.66–3.52 (m, 8H; C–H), 1.97 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), 1.89 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 170.33, 169.92, 169.09, 169.05, 153.25, 152.49, 123.43, 121.05, 100.63, 86.34, 85.22, 77.66, 71.59, 71.10, 71.62, 70.70, 70.23, 70.20, 69.50, 69.01, 68.22, 61.81, 57.01, 20.76, 20.71, 20.62, 20.60 ppm; IR (KBr): $\tilde{v}$ = 2939, 2876, 1754, 1483, 1454, 1437, 1365, 1348, 1217, 1174, 1122, 1060, 1038, 762 cm^{-1}; elemental analysis calcd (%) for C$_{27}$H$_{36}$I$_2$O$_{14}$: C 38.68, H 4.33; found: C 38.29, H 4.37.

Synthesis of glucose–PPE 2: Diyne **10** (111 mg, 0.365 mmol) and diiodide **11a** (276 mg, 0.329 mmol) were dissolved in a mixture of piperidine (0.5 mL), THF (0.5 mL), and methanol (0.5 mL) in a Schlenk flask with a flow of nitrogen and with magnetic stirring. [PdCl$_2$(PPh$_3$)$_2$] (8 mg, 0.011 mmol) and CuI (2 mg, 0.011 mmol) were added to the flask. The reaction mixture was stirred under the nitrogen at 40 °C for 16 h. The solution was slowly added to acetone (300 mL). The precipitate was washed with water. An orange solid was obtained (220 mg, 93%). The weight average molecular weight (M_w) was estimated to be 53 320 with a polydispersity (M_w/M_n) of 1.52 (eluent: DMF). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.17, 7.13, 4.95, 4.89, 4.86, 4.54, 4.46, 4.20, 4.12, 4.11, 3.86, 3.81, 3.66, 3.53, 3.44, 3.39 ppm; ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 153.75, 152.90, 117.44, 115.40, 113.63, 112.99, 103.02, 91.46, 76.88, 76.76, 73.40, 72.40, 70.24, 70.02, 69.92, 69.77, 69.12, 67.86, 61.06, 60.24, 56.35 ppm; IR (KBr): $\tilde{v}$ = 3431, 2877, 2204, 1509, 1452, 1403, 1271, 1218, 1040, 856 cm^{-1}; elemental analysis calcd (%) for C$_{36}$H$_{46}$O$_{15}$: C 60.16, H 6.45; found: C 58.89, H 6.67.

Synthesis of 6: 2,5-Diiodohydroquinone (5.05 g, 14.0 mmol) and 2-[2-(2-chloroethoxy)ethoxy]ethanol (**5**) (9.44 g, 56.1 mmol) were dissolved in DMF (30 mL). Potassium carbonate (55 g, 0.4 mol) was added to the solution. The reaction mixture was stirred under the nitrogen at the reflux temperature for 3 d. After the solution was cooled, the solid was filtered off. The solvent was evaporated and the reaction mixture was extracted with chloroform and washed with water. The organic layers were dried over MgSO$_4$ and evaporated to dryness. The solid was crystallized from acetonitrile and further purified by column chromatography (ethyl acetate/methanol 97:3). A colorless solid was obtained (2.93 g, 34%). M.p. 77–78 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.22 (s, 2H; Ar-H), 4.09 (t, J(H,H) = 4.55 Hz, 4H), 3.86 (t, J(H,H) = 4.55 Hz, 4H), 3.77 (t, J(H,H) = 4.55 Hz, 4H), 3.71 (t, J(H,H) = 4.55 Hz, 4H), 3.68 (t, J(H,H) = 4.55 Hz, 4H), 3.60 ppm (t, J(H,H) = 4.55 Hz, 4H); IR (KBr): $\tilde{v}$ = 3424, 2943, 2886, 1487, 1467, 1355, 1326, 1265, 1240, 1218, 1126, 1117, 1086, 1063, 1031, 884, 858, 835, 798 cm^{-1}; ^{13}C NMR (75 MHz, CDCl$_3$): δ = 152.76, 123.18, 86.28, 72.43, 71.07, 70.38, 70.11, 69.49, 61.64 ppm.

Synthesis of 7a: Diiodide **6** (6.26 g, 10.0 mmol) and (trimethylsilyl)ethyne (2.45 g, 25.0 mmol) were reacted in diisopropylamine/THF (1:4 v/v; 100 mL) in the presence of CuI (24 mg, 0.13 mmol), Pd(OAc)$_2$ (22 mg, 0.10 mmol) and PPh$_3$ (131 mg, 0.499 mmol). The solution was stirred overnight at room temperature. The mixture was filtered to remove the ammonium salts and the solvent was evaporated in vacuo. The solid residue was dissolved in THF (50 mL) and 1 M solution of tetrabutylammonium fluoride (in THF, 16 mL, 16 mmol) was added. The reaction mixture was stirred for 10 min at room temperature. The solvent was removed in vacuo and the product was isolated on a silica-gel column (ethyl acetate/hexanes/methanol 20:20:1). A pale-yellow solid was obtained (1.30 g, 31%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.94 (s, 2H; Ar-H), 4.09 (t, J(H,H) = 4.8 Hz, 4H), 3.81 (t, J(H,H) = 4.8 Hz, 4H), 3.71 (t, J(H,H) = 4.8 Hz, 4H), 3.62 (t, J(H,H) = 4.8 Hz, 4H), 3.54 (t, J(H,H) = 4.8 Hz, 4H), 3.32 ppm (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 153.66, 117.98, 113.28, 82.85, 79.38, 72.40, 70.92, 70.28, 69.43, 69.27, 61.56 ppm; IR (KBr): $\tilde{v}$ = 3405, 3241, 2944, 2861, 2103, 1716, 1501, 1494, 1455, 1401, 1350, 1273, 1223, 1197, 1134, 1059, 1032, 941, 862 cm^{-1}; elemental analysis calcd (%) for C$_{22}$H$_{30}$O$_8$: C 62.55, H 7.16; found: C 62.15, H 6.85.

Synthesis of (triethylene glycol)–PPE 1: Diiodide **6** was dissolved in a mixture of piperidine (0.5 mL), THF (0.5 mL), and methanol (0.5 mL) in a 25 mL Schlenk flask with a flow of nitrogen and magnetic stirring. [PdCl$_2$(PPh$_3$)$_2$] was added to the flask and the contents were treated with acetylene gas according to reference [22b]. The reaction mixture was stirred at room temperature for 16 h. The solution was slowly added to acetone (300 mL). The precipitate was washed with water. The number average molecular weight (M_N) was estimated to be 9500 with a polydispersity (M_w/M_n) of 1.85. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.16 (2H; Ar-H), 4.54 (2H; O–H), 4.20 (4H; C–H), 3.81 (4H; C–H), 3.66 (4H; C–H),

3.52 (4H; C–H), 3.45 (4H; C–H), 3.39 ppm (4H; C–H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 153.00, 117.26, 113.64, 91.54, 72.36, 70.19, 69.86, 69.01, 60.18, 60.06 ppm; IR (KBr): $\tilde{v}$ = 3426, 2928, 2871, 2204, 1514, 1426, 1353, 1278, 1216, 1127, 1062, 947, 886, 860 cm^{-1}.

Synthesis of model compound 7b: Compound **7** (312 mg, 0.500 mmol) and *p*-methoxyphenylacetylene (145 mg, 1.10 mmol) were dissolved in a mixture of piperidine (2 mL), THF (2 mL), and methanol (2 mL) in a Schlenk flask with a flow of nitrogen and with magnetic stirring. [PdCl$_2$(PPh$_3$)$_2$] (7 mg, 10 μmol) and CuI (2 mg, 10 μmol) were added to the flask. The reaction mixture was stirred under nitrogen at 40 °C for 16 h and the solvent was removed in vacuo. Water (20 mL) was added to the flask. The precipitate was collected and washed with water and ethyl acetate/hexanes mixture (1:4). A pale-yellow solid was obtained (170 mg, 54%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.44 (d, 4H; Ar–H), 7.00 (s, 2H; Ar–H), 6.85 (d, 4H; Ar–H), 4.18 (t, 4H), 3.90 (t, 4H), 3.80 (m, 10H), 3.66–3.61 (m, 8H), 3.55 ppm (t, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.70, 153.39, 132.98, 117.36, 115.35, 114.20, 113.99, 95.02, 84.45, 72.42, 71.19, 70.50, 69.75, 69.63, 61.74, 55.29 ppm; IR (KBr): $\tilde{v}$ = 3431, 2931, 2872, 1603, 1515, 1409, 1247, 1217, 1121, 1060, 1028, 833 cm^{-1}.

Synthesis of model compound 11b: Diiodide **11a** (372 mg, 0.444 mmol) and *p*-methoxyphenylacetylene (129 mg, 1.977 mmol) were placed in a small Schlenk tube. Piperidine (2 mL), THF (2 mL), and methanol (2 mL) were added under a flow of nitrogen. Magnetic stirring dissolved the starting materials, upon which [PdCl$_2$(PPh$_3$)$_2$] (7 mg, 10 μmol) and CuI (2 mg, 10 μmol) were added to the flask. The reaction mixture was stirred under nitrogen at 40 °C for 16 h and the solvent was removed in vacuo. Water (20 mL) was added to the flask. The precipitate was collected and washed with water and ethyl acetate/hexanes mixture (1:3). A pale-yellow solid was obtained (190 mg, 63%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.44 (d, 4H; Ar–H), 6.99 (s, 1H; Ar–H), 6.93 (s, 1H; Ar–H), 6.83 (d, 4H; Ar–H), 4.24 (d, 1H), 4.12 (m, 2H), 3.87–3.73, 3.62–3.42, 3.32 (t, 1H), 3.24 ppm (d, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.68, 152.98, 133.14, 117.70, 114.09, 113.95, 113.31, 103.01, 95.02, 84.63, 76.33, 75.63, 73.28, 72.89, 70.89, 70.30, 70.14, 69.60, 69.49, 68.70, 61.51, 56.34, 55.30, 55.25 ppm; IR (KBr): $\tilde{v}$ = 3418, 2933, 1603, 1515, 1404, 1248, 1218, 1171, 1030, 832 cm^{-1}.

Acknowledgement

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