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Redox-Active Peptide Functionalized Quinquethiophene Based Electrochromic π-Gel

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Abstract: Here, we report an electrochromic system based on self-assembled dipeptide 8 appended redox active quinquethiophene π -gel. The designed peptide-quinquethiophene consists 9 of a symmetric bolaamphiphile that has two segments: a redox active π -conjugated 10 quinquethiophene core for electrochromism and peptide-motif for the involvement of molecular 11 self-assembly. Investigations reveal that self-assembly and electrochromic properties of the π -gel 12 are strongly dependent on the relative orientation of peptidic and quinquethiophene scaffolds in 13 14 the self-assembling system. The colors of the π -gel film are very stable with fast and controlled switching speed at room temperature. 15

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24 Introduction

A variety of biomolecules such as peptides,^[1-2] carbohydrates,^[3-5] nucleobases^[6-7] and 25 nucleotides^[8] have been functionalized with semiconducting organic π -conjugated system 26 27 for the synthesis of self-assembled nanostructures which have been used in the electronics.^[9-13] Oligothiophene,^[14-18] development of supramolecular oligo(*p*-28 phenylenevinylene) (OPV),^[19-20] diacetylene (DA),^[21] benzo[ghi]perylene monoimide 29 (BPI),^[22] naphthalene diimide (NDI)^[23] and perylene diimide (PDI)^[24-26] have been 30 conjugated with various peptide motifs. Ubiquitously, the main objective is to assemble 31 32 π -conjugated units into a highly-ordered superstructure for effective charge-carrier mobility.^[27] Aromatic π -conjugated aromatic cores at the centre functionalized with 33 backbones self-assemble into interesting functional supramolecular additional 34 architectures.^[28-30] The π -conjugated motifs have tendency to form supramolecular 35 hierarchical functional nanostructures in a suitable solvent called as π -gels, which was 36 reported first time by Ajayaghosh *et al.*^[31] Thereafter, the class of π -gels were reported 37 38 and probed tremendously owing to their potential applications in material sciences including organic electronics, sensing, OLED, energy harvesting systems, memory effect, 39 and imaging probes.^[31-34] The structural correlations in the development of self-40 assembling systems were also studied.^[35-36] Among the large number of extended π -41 conjugated systems, oligothiophene is one of the most studied molecules owing to their 42 relatively high conductivity, chemical stability, solubility and processability. To date, a 43 number of self-assembled peptide-oligothiophene conjugated systems have been reported. 44 Baeuerle et al. described a peptide-oligothiophene conjugate composed of a head-to-tail 45 coupled tetra(3-hexylthiophene) and a silk-inspired GlyAlaGlyAlaGly (GAGAG) 46

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pentapeptide sequence.^[37] The oligothiophene conjugated pentapeptide undergoes 47 directed hydrogen bonding interactions and self-organization which lead to novel two-48 dimensional (2D) and three-dimensional (3D) nanoscale structures. Tovar et al. reported 49 peptides bearing internal π -conjugated segments (bithiophene) that self-assembled into 50 one-dimensional (1D) nanostructures in completely aqueous and physiologically relevant 51 environments.^[38] Schenning *et al.* described the chiroptical properties of a series of chiral 52 oligo(ethylene oxide) functionalized π -conjugated self-assembled quinque-, sexi-, and 53 septithiophenes.^[39] 54 Stupp *et al.* reported self-assembly of quinquethiophenes functionalized with β -sheet forming peptide, which formed 1D nanostructure in aqueous 55 solution.^[40] Successful applications of electrochromic devices (ECD)^[41-44] include smart 56 sunglasses,^[45-46] smart-window,^[47-49] stretchable electronic skin,^[50] and electrochromic 57 display devices.^[51] Among the varieties of small molecular and polymeric organic 58 electrochromic materials used in electrochromic devices, oligothiophenes as well as 59 polythiophene derivatives are an important class of π -conjugated organic material.^[52-56] 60 Thiophene-based oligomers and polymers possess intrinsic contrasting colours between 61 the neutral and oxidized forms concomitant with forming stable intermediates.^[57-60] 62 Moreover, polythiophenes exhibit several additional advantages including well defined 63 molecular backbone, solution processability, precise molecular ordering and crystallinity 64 65 for superior charge transfer. The molecular structure is a key factor for molecular packing induced by several non-covalent interactions, which influence the morphology of 66 materials. Morphology strongly influences the material properties and performance of 67 68 devices. Hence, the molecular structure of electrochromic materials and packing capability are the crucial factors for the fabrication of good functional material. 69

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70 Here, we report the design, synthesis and self-assembly study of peptidequinquethiophene based π -gel, which exhibits electrochromic property. Functionalization of 71 peptide-segment into oligothiophene unit provides two significant effects (i) π -conjugated 72 peptide capable to form supramolecular π -gel and (ii) easy solution processability of 73 oligothiophene derivative unlike polymeric electrochromic materials. A dipeptide-functionalized 74 quinquethiophene based bolaamphiphile (compound 1, L = Leu) was synthesized (Figure 1, 75 Scheme S1-S2). The designed compound has two backbone segments (i) a redox active π -76 77 conjugated quinquethiophene (5t) core responsible for electrochromism and (ii) set of dipeptide motifs for the participation in molecular self-assembly. Polar functional end groups (carboxylic 78 acid) are adopted as a controlling unit for self-assembly of π -conjugated cores in aqueous phase. 79 80 The self-assembly and electrochromism of compound 1 were studied in aqueous phase through π -gel formation. The peptide-quinquethiophene conjugate *i.e.* compound 1 yields a pH-81 responsive self-supporting π -gel (Figure 1 and Figure S1). 82



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Figure 1. Molecular structure of compound 1 and schematic representation of the gelation mechanism. The peptide-quinquethiophene motifs self-assemble into a supramolecular sheet arrangement through hydrogen-bonding and π - π stacking interactions. The self-assembly process leads to the formation of nanofibrils in water, consequently into π -gel.

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10.1002/asia.201701460

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88 **Results and Discussion**

89 Diverse spectroscopic, optical and microscopic techniques have been performed to investigate the self-assembly behaviour of π -gel of compound 1. The critical gelation 90 concentration (CGC) of self-supporting π -gel **1** is 16 mmol L⁻¹. The π -gel turns into 91 solution at 82 °C. The gelation melting temperature ($T_{gel} = 82$ °C) was determined and 92 confirmed by the inverted test tube method.^[61-63] Rheological measurements were carried 93 out to measure viscoelastic preferences of the π -gel 1 (at $C = 20 \text{ mmol } L^{-1}$). It is obvious 94 that any soft material is highly sensitive towards applied force and as a result it flows 95 96 against applied stress. In frequency sweep experiments (the proposed strain = 0.1%; which was kept constant throughout the experiment), the storage (G') and loss (G'') 97 module parameters show a wide plateau region over the applied frequency (Hz) and do 98 99 not intersect each other up to 100 Hz frequency (Figure S2). Moreover, the elastic 100 modulus G' shows a greater value than the viscous modulus G" over the frequency range of the experiments. From this study, it is clear that the supramolecular gel of compound 1 101 102 has the capability to show enough tolerance towards external forces with sufficient strength implies its characteristic semi-solid type behaviour.^[64] The self-assembled 103 nanostructural morphology of gel matrix was analyzed using transmission electron 104 microscopy (TEM). TEM image of π -gel 1 revealed the formation of nanofibrous 105 106 morphology (Figure S3). The average width of the fibers is found to be 45 nm with several micrometres in length. Thus, the aggregation of these entangled fibers would be 107 immobilised surrounding molecules 108 the water to produce a self-supporting supramolecular gel. 109

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Dilute solution of compound 1 (1.56 \times 10⁻⁵ M) shows an absorption maximum at 386 nm. π -Gel 110 1 display $(1 \times 10^{-3} \text{ M})$ an intense absorption maximum at 410 nm (Figure 2a). The absorption 111 maximum of the aqueous gel state red-shifted about 24 nm compared to that of typical solution 112 state absorption. Upon dilution, the intensity of the absorption peak blue shifted, which signifies 113 the formation of self-assembled J-aggregate.^[65] This band could be originated due to π - π * 114 transition of π -conjugated quinquethiophene backbone. Fluorescence properties of compound 1 115 116 were also measured for both states (gel state and solution state) to establish gelation 117 phenomenon. An aqueous solution of compound 1 shows emission band at 586 nm with a shoulder at 550 nm whereas the corresponding π -gel displays only a broad peak around 590 nm. 118 119 The above changes with small red shift in emission spectra may be attributed due to the molecular association of peptide-quinquethiophene. Simultaneously, in addition to the small red 120 shift, fluorescence quenching is also observed for π -gel 1 in comparison with emission maxima 121 of its aqueous solution (Figure 2b). In addition, the fluorescence quenching signifies the 122 molecular stacking of quinquethiophene cores via π - π stacking interactions by which peptide-123 quinquethiophene scaffolds undergo J-type of aggregation eventually to form a self-supporting 124 gel.^[66-67] 125

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Figure 2. (a) UV-Vis spectra of compound **1** at different concentrations and (b) fluorescence spectra of compound **1** in aqueous medium (pH = 10) and gel state (pH = 7.2); the excitation wavelength $\lambda_{max} = 410$ nm. Temperature dependent CD spectra of aqueous solution of compound **1** (pH = 7.2) (c) upon heating, and (d) upon cooling (*C* = 200 µM).

132 To understand conformational preferences of self-assembled peptide-quinquethiophene motifs in the hydrogel, we performed FTIR spectroscopy experiments on both states of 133 compound 1 (gel and solid states; Figure S4). Compound 1 in the solid state produced 134 135 characteristic amide A band (N-H stretching) at 3453 cm⁻¹, indicating free amide-NH 136 groups. While, in the gel state, all the amide-NH groups are engaged in hydrogen-bond interactions since the corresponding band is shifted to 3300 cm⁻¹. In comparison with the 137 solid of compound 1, FT-IR peaks for the amide-NH and C=O groups significantly 138 139 become broad in the self-assembled gel matrix. Additionally, compound 1 in the solid

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state displays characteristic amide I and amide II bands at 1653 cm⁻¹ and 1618 cm⁻¹ along 140 with an intense amide II (N-H bending) band centered at 1554 cm⁻¹. The corresponding 141 bands of compound **1** shifted to 1660 cm⁻¹, 1633 cm⁻¹ and 1546 cm⁻¹ in the hydrogel state. 142 The significant shift of amide I band from 1653 cm⁻¹ to 1660 cm⁻¹ supports a 143 conformational change from unordered structure to supramolecular helical structure by 144 peptidic segment during self-assembly in the gel matrix.^[68] This characteristic observation 145 is also corroborated with CD spectroscopy. Circular dichroism (CD) was used to 146 scrutinise the supramolecular-aggregation preferences of self-assembled compound 1. 147 Hydrogel of compound 1 shows strong CD absorption bands in the range of 350-550 nm 148 primarily with a bisignated Cotton effect (Figure 2c).^[40] This strong CD pattern originates 149 from the relative orientation of quinquethiophene core. A set of small intense positive CD 150 151 bands (around 219 and 255 nm) are also observed which signifies a chiral propensity of the peptide-backbone. The CD spectrum featured with a strong negative CD signature at 152 480 nm and a positive CD signature at 416 nm along with a crossover point located near 153 154 444 nm. It is worth mentioning that the oligothiophene segment is orientated in a welldefined distinguished orientation in space as the crossover point in CD spectra and the 155 absorption maximum in UV-Vis spectroscopy are close to each other.^[69-70] The peptide-156 quinquethiophene motifs undergo association using π - π stacking and intermolecular 157 hydrogen-bonding interactions, which consequently produce chiral supramolecular 158 aggregates.^[66] Furthermore, to investigate conformational preferences of the self-159 assembling systems and temperature effect on these self-assembling systems, we 160 161 performed a variable-temperature CD spectroscopy (Figure 2c and 2d). The peptidic 162 segments of π -gelator **1** adopt supramolecular β -sheet type of conformation as it is

evident from the associated CD bands at 219 nm. CD band at 219 nm ascribed to the n- π^* 163 transition of the amide group and another band at 255 nm attributed due to higher energy 164 absorption of the thiophene motif in the representative CD spectra at 25 °C. The intensity 165 of the bisignated CD bands at quinquethiophene region decreases upon heating (from 25 166 °C to 85 °C) and subsequently increases upon cooling. Moreover, the amide region is also 167 168 accompanied the similar trend in the typical CD investigation (Figure 2c). While the temperature of the aqueous π -gel **1** is cool down from 85 °C to 25 °C, the bisignated CD 169 170 band shows an enhancement in its intensity (Figure 2d). This study demonstrates that the π - π stacking interactions between thiophene motifs and non-covalent hydrogen bonding 171 interactions between peptidic segments play a vital role to accomplish a self-assembling 172 system in the π -gel. Upon heating, both type of interactions weaken, as indicated by 173 smaller CD intensity at amide and thiophene regions. Moreover, these two significant 174 interactions would not control on each other and unitedly they participate in stabilising 175 the self-assembling motifs. At higher temperature, a substantial CD signal was obtained 176 even at 85 °C. It is expected that all aggregates will be converted into the monomer. 177 However, soluble aggregates remain even at 85 °C due to the presence of peptide 178 backbone attached with quinquithiophene core. Hydrogen bonding and π - π stacking 179 interactions among the gelator molecules drive toward the formation of soluble 180 aggregates even at 85 °C. The aggregated-motifs further associated into higher ordered 181 chiral supramolecular assemblies. The presence of chiral residual amino acid and 182 molecular atropisomerism around thiophene residues induce chiral assemblies.^[71] A 183 possible mechanism determine the self-assembling pattern peptide-184 to of 185 quinquethiophene moieties in compound **1** is proposed (Figure 1).

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186 The redox properties of oligothiophenes conjugated peptide were measured by using cyclic voltammetry (CV). Figure 3a demonstrates cyclic voltammetry investigations of π -gel 1 187 placed between two ITO glasses. π -Gel 1 shows the oxidation potential at 1.21 V and the 188 corresponding reduction peak at 0.58 V. This significant CV scheme implies the successive 189 190 formation of a cation radical as well as a dication adduct by compound 1 during oxidation. The 191 oxidation potentials exhibited by π -gel are comparable to those reported potentials of oligothiophene derivatives.^[72-74] This redox responsive colorimetric alterations could be 192 193 reproducible by repetitive scanning schemes (Figure 3b), since the extended π -conjugated 194 oligothiophene core can stabilize the formed oxidized-species. The electrochromic response can 195 also be observed from the π -gel film of compound **1** coated on an ITO glass electrode (Figure 3c, Scheme 1). Electrochromic device fabrication process is depicted in Scheme 1. Apparently, an 196 electrochemical reaction can alter the colours of the π -gel-film from yellow to colorless (Scheme 197 1). CV for the solution of compound 1 was performed by placing aqueous solution of compound 198 1 as active layer in between two ITO glasses. Surprisingly, the solution of compound 1 failed to 199 200 display electrochromism property over a wide range of operating voltages. Other 201 quinquethiophene (5T) motif (compound 6) also failed to show electrochromism behaviour. However, compound 1 in aqueous solution and compound 6 in CH_2Cl_2 show redox potentials in 202 their individual CV measurements (Figure S5). Peptide functionalized quinquithiophene based 203 supramolecular π -gel 1 is responsible for electrochromism. 204



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Figure 3. Cyclic voltammograms of π -gel 1 placed between two ITO glass plates with (a) scan rate of 25, 50, 100 and 200 mVs⁻¹ and (b) at continuous scanning mode. (c) Reversible color change of π -gel 1 coated on ITO glass plate at operating voltage (50 mVs⁻¹) of 0.6 V (yellow color) and 1.21 V (colorless).



212 Scheme 1. (a) Scheme for device fabrication process. (b) Electrochromic test of the prepared device of π -213 gel film. Chemistry - An Asian Journal

10.1002/asia.201701460

214 Conclusions

215 In summary, we have described the electrochromic properties of a quinquethiophene conjugated self-assembling dipeptide functionalized bolaamphiphile π -gel. Self-assembly 216 217 and electrochromic properties of compound 1 are strongly dependent on the relative 218 orientation of peptides and quinquethiophene cores. Concentration dependent UV-Vis 219 data support the formation of J-aggregates. FTIR and CD spectroscopic studies reveal the 220 vital role of hydrogen bonding and π - π stacking interactions in the supramolecular π -gel. 221 Variable temperature dependent CD investigations evidently demonstrate the contribution 222 of hydrogen bonding and π - π stacking interactions in the event of stabilisation of selfassembling system. Microscopic measurements distinctly shows the formation of nano-223 224 fibrillar structures in the gel. Electronically conjugated quinquethiophenes facilitate the charge conduction efficiently using π -orbitals via overlapping with adjacent molecules. 225 226 Owing to the presence of a redox active quinquethiophene (5t) motif as core backbone in the π -gel 1, the corresponding supramolecular π -gel exhibits electrochromism. Solutions 227 of compound 1 as well as quinquithiophene core don't exhibit electrochromism. Due to 228 229 the presence of strong hydrogen bonding and π - π stacking interactions among peptide functionalized quinquethiophene motifs, the supramolecular π -gel 230 **1** exhibits electrochromism. The optical properties of hydrogel 1 coated on ITO glass electrode can 231 be controlled by the applied potential, which signifies its colorimetric response upon 232 233 redox reactions.

- 234 **Experimental Section**
- 235 General Methods and Materials:

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236 Amino acids, thiophene, *n*-butyl lithium (1.6 M in hexane), tributyltin chloride, 2,5-dibromo-3-237 methylthiophene, 5-bromo-2-thiophenecarboxylic acid, tetrakistriphenylphosphine palladium(0), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), 4 - (N.N -238 citric acid. 239 dimethylamino)pyridine, tert-butyl alcohol, trifluoroacetic acid, 1-hydroxybenzotriazole (HOBt), acetonitrile, tetrabutylammonium perchlorate (Bu₄NClO₄) were obtained commercially. 240 241 Tetrahydrofuran (THF) was dried over Na/benzophenone and distilled prior to use. Indium tin oxide (ITO) coated quartz glass substrates (10 mm \times 10 mm) with thickness about 150 nm were 242 purchased from J. K. Impex, Mumbai. 243

244 FT-IR spectroscopy

FTIR spectra of powder sample and gel were measured using Bruker (Tensor 27) FT-IR spectrophotometer. Samples were prepared in milli-Q water and scanned from 400 to 4000 cm⁻¹.

247 Circular Dichroism (CD) spectroscopy

Circular dichroism (CD) spectra were obtained on a Jasco J-815 spectropolarimeter. Spectra were measured between 600 to 195 nm with 0.1 nm data pitch, 1 nm bandwidth, 20 nm min⁻¹ scanning speed and a response time of 4 s. Samples were prepared by diluting peptidequinquethiophene bolaamphiphile hydrogel of 20 mmol L⁻¹ in milli-Q water to get final concentration of 200 μ M.

253 UV-Vis Spectroscopy

UV-Vis absorption spectrum of the π -gel was recorded using a Varian Cary100 Bio UV-Vis spectrophotometer. Samples were diluted in different concentrations and the experiments were conducted.

257 Fluorescence Spectroscopy

Fluorescence spectra of compound **1** and π -gel **1** (20 mmol L⁻¹) were recorded on a Horiba Scientific Fluoromax-4 spectrophotometer with 1 cm path length quartz cell at 25 °C. The slit width for the excitation and emission was set at 2 nm and a 1 nm data pitch. Excitation of gel sample was performed at 410 nm.

262 Transmission electron microscopic (TEM) study

Transmission electron microscopic images were taken using a PHILIPS electron microscope (model: CM 200) operated at an accelerating voltage of 200kV. Hydrogel (20 mmol L^{-1}) solution was diluted to 1 mmol L^{-1} in milli-Q water and dried on carbon-coated copper grids (300 mesh) by slow evaporation in air, then allowed to dry separately in a vacuum at room temperature.

267 **Rheology**

The experiment was done on an Anton Paar Physica Modular Compact Rheometer (MCR 301, Austria). Oscillating rheology was used to quantify the mechanical properties of the π -gel of compound **1**. Gel sample for rheology experiment was prepared (20 mmol L⁻¹) in milli-Q water. A 25 mm cone plate with 1° angle configuration was used and the temperature was set to be constant at 25 °C. Storage (G') and loss (G'') moduli were measured at 0.1% strain with a true gap of 0.05 mm.

274 Electrochemical measurements

275 Cyclic voltammetry (CV) was performed using an AUTOLAB/PG STAT302N and a three-276 electrode cell equipped with platinum working, platinum counter and an Ag/AgCl reference 277 electrodes. Bu₄NClO₄/CH₂Cl₂ (0.1 M) was used as supporting electrolyte. In a typical 278 electrochromic test, a thin film of π -gel material was prepared by placing/dispersing the gel 279 material and then sandwiched between two ITO coated glasses (3 × 3 cm). Thick double-sided

sellotape was used as appropriate spacer between the ITO glass pair-gel sandwiches to prevent flow of the gel from the system. The ITO coated glass typically employed as a working electrode. Pt and Ag/AgCl were used as counter electrode and reference electrode respectively. For control experiments, aqueous solution of compound 1 and dichloromethane solution of compound 6 were placed between two ITO coated glasses and CV as well as electrochomism experiments were performed respectively.

286 NMR spectroscopy

All NMR characterizations were carried out on a Bruker AV 400 MHz spectrometer at 298 K. Compound concentrations were in the range 5-10 mmol L⁻¹ in CDCl₃ and (CD₃)₂SO. Chemical shifts were expressed in parts per million (ppm, δ) relative to residual solvent protons as internal standards (CHCl₃: δ 7.26, DMSO: 2.50 for ¹H NMR, CHCl₃: δ 77.00, DMSO: 39.50 for ¹³C NMR). ¹H NMR multiplicities were designated as singlet (s), doublet (d), triplet (t), quartet (q) multiplet (m) and broad singlet (bs).

293 Mass spectrometry

294 Mass spectra were recorded on a Bruker micrOTOF-Q II by positive mode electrospray 295 ionization.

296 **Preparation of** π **-gel**

19 mg of compound **1** (20 mmol L⁻¹) was suspended in 0.9 mL water. The pH of the compound– water mixture was first increased to pH = 10 by slow addition of 0.5 M NaOH to get a clear peptide-water solution, and then the pH of the system gradually decreased by slow addition of 0.1 M HCl. At pH~7.2, the peptide-water system turned into a self-supporting π -gel, which was confirmed by test-tube inversion method. To determine the gelation temperature (T_{gel}), a sample

vial of compound 1 gel ($C = 16 \text{ mmol } L^{-1}$) was immersed in an oil-bath and the temperature was 302 slowly increased at a rate of 2 °C per 5 min. 303 Acknowledgements 304 AKD sincerely acknowledges NanoMission, Department of Science & Technology (Project No. 305 SR/NM/NS-1458/2014), New Delhi, India for financial support. SIC, IIT Indore is 306 acknowledged for providing access to the instrumentation. MK is thankful to IIT Indore for his 307 308 postdoctoral research fellowship. We thank Dr. Manoj Manna for his generous help in doing the electrochromism experiments. 309 **Keywords**: 310 self-assembly, peptide-quinquethiophene, electrochromism 311 312 Notes and references information available 313 Supporting for this article is on the WWW under 314 http://dx.doi.org/10.1002/asia.201xxxxxx 315

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Reduction

.21

colorless



-0.5

463

Text for Table of Contents: An electrochromic system based on self-assembled dipeptide 464 appended redox active quinquethiophene hydrogel is developed and the hydrogel device film 465 displays colorimetric response against applied potential (V) which is very stable with fast and 466 controlled switching speed at room temperature. 467

0.5 Potential (V)

0.58

0.0

0.80

1.5

1.0