Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Functionalized Conducting Polymer Materials Toward Molecular Device

T. Shimidzu [a]

[a] Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto, 606, Japan

Version of record first published: 04 Oct 2006.

To cite this article: T. Shimidzu (1990): Functionalized Conducting Polymer Materials Toward Molecular Device, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 190:1, 75-83

To link to this article: http://dx.doi.org/10.1080/00268949008047834

Mol. Cryst. Liq. Cryst., 1990, Vol. 190, pp. 75–83
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Functionalized Conducting Polymer Materials Toward Molecular Device

T. SHIMIDZU

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, JAPAN

This paper involves three real approaches to constitute functional molecular materials toward molecular devices: (1) Method to materialize various functional molecules with conducting polymer matrix which conveys and reflects electronic structure and states of these molecules: The resulting functional molecule incorporating conducting polymer materials showed characteristic functionalities caused by those incorporated molecules. (2) Ultramicro-fabrications of conducting polymers, by LB method, by electrochemical copolymerization method, and photochemical polymerization method: They provided us an ultra-high anisotropic conducting and insulating alternative multi-layers, a nm level depth profile controlled conducting copolymer multi-layers, and 2D, 3D conducting polymer network fabrication. (3) Multifunctionalization of functional molecule to be incorporated in molecular materials: A few multi-mode chemical signal transducer molecule which can respond to multi-mode stimulations were designed and demonstrated.

INTRODUCTION

There are many molecules and they have their own specific functions. For their exploitation through materialization, conducting polymers are considered as a suitable matrix, for its electron conductive property is to be used to prove the electronic structure and state which relate directly functions of these molecules. To construct molecular device, the fabrication and materialization of those functional molecules in molecular level is one of the most important problems, in advance. The concept of the functional molecular material in which molecular device is to be included is illustrated in Figure 1.

The present study demonstrates three approaches toward molecular device construction, in practice, with (1) materialization of functional molecules with conducting polymer by their incorporations, (2) ultra-thin and molecular level fabrication of conducting polymers, (3) multi-functionalization of functional molecules to be incorporated in the functional molecular material and molecular device.

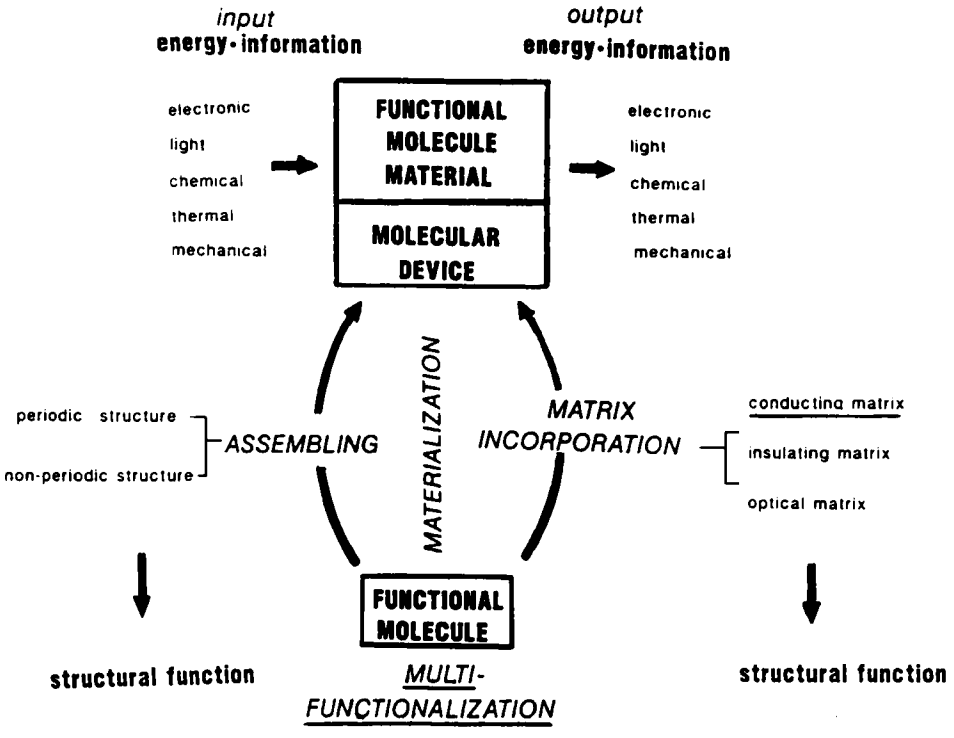
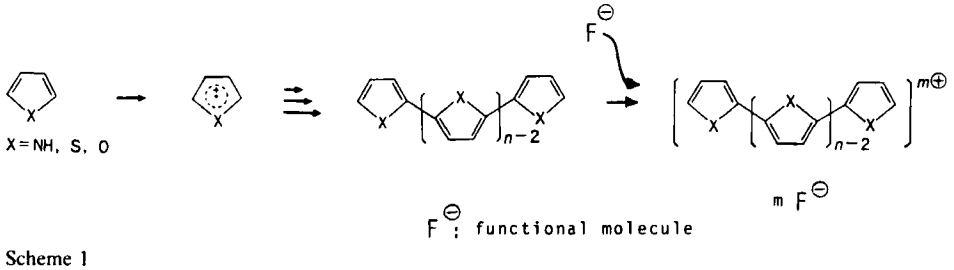


FIGURE 1 Concept of functional molecular materials toward molecular devices.

1. Materializations functional molecules by their incorporation in conducting polymers

Materialization of functional molecules by incorporation of functional molecules in a conducting polymer matrix is achieved by electrolytic polymerization of pyrrole, thiophene, aniline, furan, etc., in the presence of negatively charged functional molecules.[1-4] The incorporation of the functional molecules is driven electrostatistically by the positive charges of the partially oxidized conducting polymer matrices through a doping process, as shown in the Scheme 1.



Scheme 1

SCHEME 1

Electrolytic polymerization of the monomer was achieved in the presence of the negatively charged functional molecules. A key concept of this preparative approach is that the resulting conducting polymer has a lower redox potential (doping and undoping) than its monomer, therefore anodic doping occurs simultaneously with electropolymerization. An electrolyte anion or anionic functional molecule is incorporated into the partially oxidized conducting polymer matrix so as to conserve its electroneutrality.

The resulting functionalized conducting polymers display the specific and distinguished functions which were caused by the incorporated functional molecules. Also, the conductivity of the conducting polymer matrix was not much reduced. Table I shows functionalities of the functional molecule incorporating conducting polymer materials, as examples.

The functionalities of the resulting functionalized conducting polymer materials are electrochromism,[1-5] photoelectric conversion,[1-4] electrogenarated chemiluminescence,[2,6] highly dispersed noble metal,[1-3] charge-controllable membrane,[6-12] sensor,[1-3] polymer battery,[13-14] etc.

The incorporated functional molecule is exchanged by electrochemical reduction and thereafter reoxidation in the presence of a replacing functional molecule. Applying this method to the polyanion doped conducting polymer, also positively charge functional molecule can be incorporated by a pseud-cathodic doping process. The incorporation is occurred when the polyanion doped conducting polymer is electrochemically reduced at which the molecularly hybridized polyanion attracts the positively charged functional molecule.

Chemical polymerizations are also useful methods to prepare functionalized conducting polymer materials. Matrix supporting method,[3] vapor phase polymerization

TABLE I

Functions of Functional Molecule Incorporating Conductive Polymers

Functional dopant/matrix [a]	Charge	Function	Procedure [b]
Anthraquinone 2-sulphonate	Sulphonate	Electrochromism	1, 3
$Lu(PTS)_2$	Sulphonate	Electrochromism	1, 3
$Fe(BPS)_n(BP)_{3-n}$	Sulphonate	Electrochromism	1, 3
$Ru(BPS)_n(BP)_{3-n}$	Sulphonate	Electrochemiluminescence	1, 3
$MTPPS_4$ (M = Zn, Pd, etc.)	Sulphonate	Photosensitized electrode	1, 3
MTMPyP	Pyridinum	Photosensitized electrode	2
Rose bengal	Carboxylate	Photosensitized electrode	1, 3
Indigo carmine	Sulphonate	Photosensitized electrode	1, 3
Poly(vinyl sulphate)	Sulphate	Charge-controllable membrane	1, 3
Poly(styrene sulphonate)	Sulphonate	Charge-controllable membrane	1, 3
Nafion®	Sulphonate	Charge-controllable membrane	1, 4
Polynucleotide	Phosphate	Nucleic acid sensor	1, 3
Nucleotide	Phosphate	Nucleic acid sensor	1, 3
Porous filter	-	Filtration	4
Phosphotungstate	Heteropoly acid	Electrochromism	1
$PtCl_4^{2-}$	$PtCl_4^{2-}$	Highly dispersed metal	1, 3
$AuCl_4^-$	$AuCl_4^-$	Highly dispersed metal	1, 3

[a] PTS = phthalocyanine tetrasulphonate; BP = bathophenanthroline; BPS = BP disulphonate; $TPPS_4$ = tetra(4-sulphophenyl)porphyrin; TMPyP = tetra(4-methylpyridyl)porphyrin.

[b] Incorporation procedure: 1, electrochemical anodic doping; 2, electrochemical pseudo-cathodic doping; 3, vapour-liquid interface chemical polymerization; 4, bulk chemical polymerization.

method[15] and catalytic method[16] were demonstrated. The matrix support method is illustrated in Table II. In these methods, all kinds of functional molecules (negatively charged, positively charged, and neutral) can be incorporated.

Utilizing those functionalized conducting polymers, many kinds of functional materials whose functions are caused by the incorporated functional molecules are easily constructed, in principle.

2. Molecular level and ultrathin-fabrications of conducting polymers

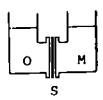
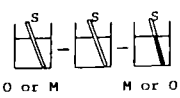
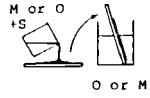
2-1. Electrochemical Polymerizations of Langmuir-Blodgett Multilayers of Amphiphilic Pyrrole Derivatives.[16-18]

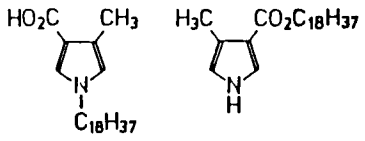
Amphiphilic pyrrole derivatives such as CPy and EPy shown in Figure 2 give very stable LB monolayers on a neutral subphase, especially with n-octadecane in the ratio of ca. 2/1. The collapse pressure reached up to 50 mN/m. More than 600 layers could be transferred onto the hydrophobic substrates, silated ITO-deposited glass and ITO-deposited polyester film, as Y-type films. The oxidative electropolymerization of the 200 layers of mixed EPy—n-octadecane (2:1) on ITO-deposited substrate was carried out under a condition in $LiClO_4$ containing acetonitrile, in which only the lower tip of the monomeric LB multi-layers was dipped in the electrolyte solution (Figure 3). The region of the monomeric LB multilayers under the liquid surface did not polymerize but dissolved in the solution. After an amorphous conducting polymer was given at the lower tip, then the polymerization began near the liquid surface and proceeded upwards. The polymerization was observed by the change in color of the multi-layers from transparent to reddish brown.

The colored area was confirmed to be polymer of the amphiphilic derivative of pyrrole, spectroscopically. The electropolymerization of the LB multi-layers was also attempted in acetonitrile-$LiBF_4$ and acetic acid-$LiClO_4$. The present polymerization occurred topochemically. The polymerization proceeded at the point of contact with the pyrrole derivative to the front of the electropolymerized region, as can be seen in Figure 3. Both X-ray diffraction analysis and TEM image of the cross section showed fine multi-layered structure. A clear image of the layered structure indicates that the present preparation method allows molecular regulation of the structure of conducting polymer material on a wide range up to nm level

TABLE II

Chemical Preparation Methods of Conducting Polymer Composites

Chemical polymerization	SEPTAL 	DIPPING 	BLENDING 
Monomer (M)	pyrrole, thiophene, furan, aniline, indole, their derivatives		
Support (S)	ion-exchange membrane, natural and synthetic membrane, porous glass, porous ceramics		
Oxidant (O)	Lewis acid, halogen, peroxide, metal acid		
Solvent	water, organic solvent, gas-phase reaction		



CPy EPy

FIGURE 2 Amphiphilic Pyrrole derivatives.

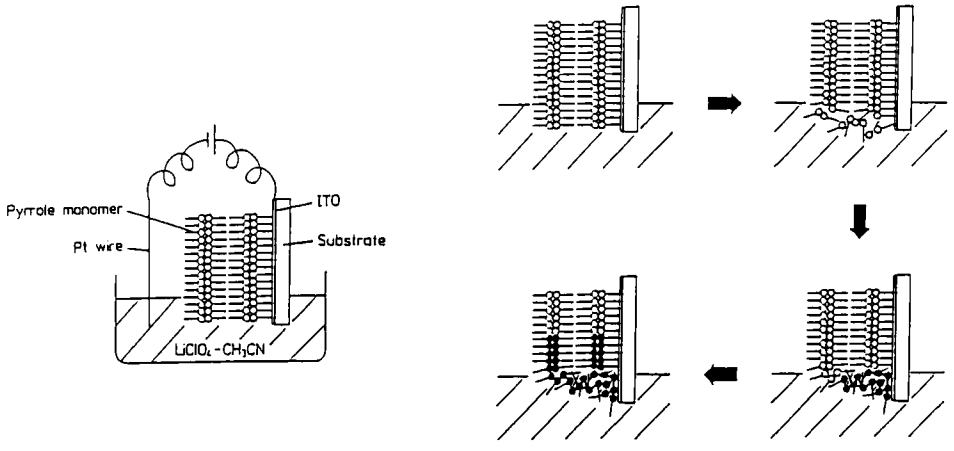


FIGURE 3 Electrolytic polymerization of the LB multi-layers.

as is seen in Figure 4. The dark region is considered to be polypyrrole moiety, while the light region is alkyl chain one. The bilayer d spacing is 55-62 A, almost same as that obtained by X-ray diffraction analysis.

The present electropolymerized LB multi-layers had a highly anisotropic dc-conductivity by ca. 10 orders ($\sigma_{\parallel} = 10^{-1}$ S/cm, $\sigma_{\perp} = 10^{-11}$ S/cm), as is speculated from its layered structure. The dc conductivity parallel to a multi-layers ($\sigma_{\parallel}$) was measured by the four-electrode method. The dc conductivity in the perpendicular direction ($\sigma_{\perp}$) was measured by putting the multi-layers between two ITO electrodes.

2-2. Depth Profile Control of Different Conducting Polymer Multi-layers in Sub-nanometer Level.[4]

Utilizing electrocopolymerization technique, various multi-layers of conducting copolymer were constructed. The copolymer composition and the thickness of the polymerized copolymer deposited on the electrode are easily controlled by the potential in the electrocopolymerization process. The electrocopolymerizations were carried out with occasional step potential changes.

As is shown in Figure 5, finely hetero-layered structures of polypyrrole and poly(pyrrole-co-3-methylthiophene) at sub-nanometer level were observed by TEM

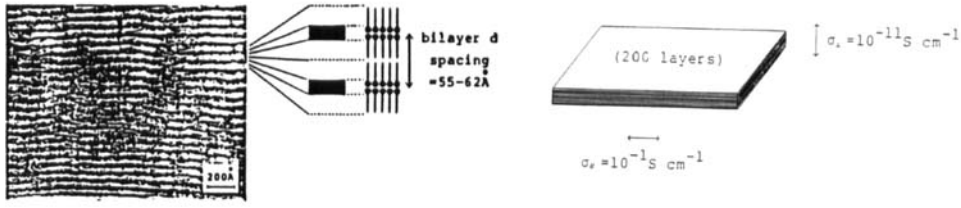


FIGURE 4 TEM picture of the cross section of the electropolymerized EPy-octadecane LB multilayers (Left) and its anisotropic conductivity (Right).

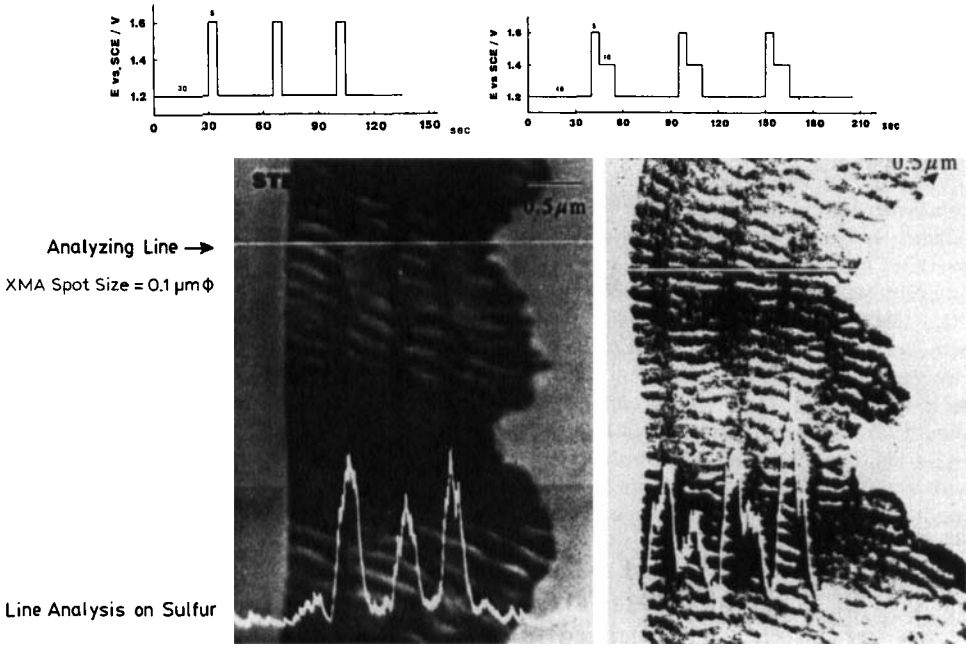


FIGURE 5 Potential sweeps, STEM image and XMA analyses of conducting polymer hetero layers prepared by electrocopolymerization of pyrrole and 3-methylthiophene.

picture of the cross section of the resulting conducting multi-heterolayers and the copolymer composition analyzed for the sulphur content from 3-methylthiophene component by X-ray micro—elementary analysis (XMA). In addition, both Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) data (Figure 6) proved an alternative multi-heterolayered structure in sub-nanometer level.

The resulting multi-layers correspond exactly with the step potential of the electrocopolymerization, that is, the monomer composition in the resulting copolymer was governed by the charge potential, and a clear interface was observed. These results suggest that this convenient electrocopolymerization provides a useful method to fabricate finely and structurally controlled conducting multi-heterolayers, and

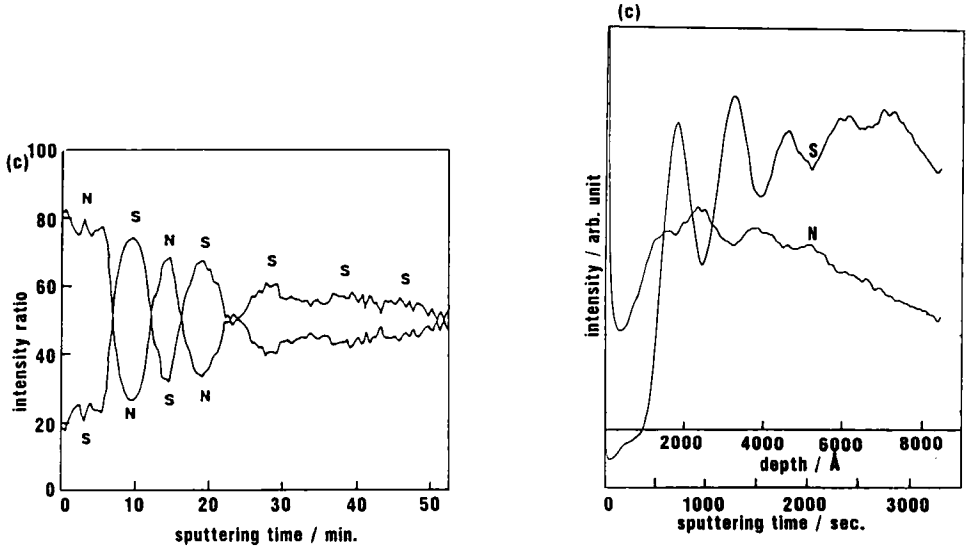


FIGURE 6 Depth profiles of the conducting polymer heterolayers by AES (Left) and SIMS (Right).

the resulting ultra-thin heterolayered material should take an important place in both electronic and optical devices, to be compared with an ultra-thin or a super layer (super lattice) of a semiconductor, and will provide a novel organic conducting material having a controlled quantum well and quantum functionality.

2-3. *Patterning of 2D, 3D Conducting Polymer Networks*[4,19,20]

Fabrications of conducting polymer network is considered to be one of the most important subject in the field of molecular electronic devices. A novel photo-sensitized polymerization of pyrrole was investigated in order to form fine conducting polymer pattern on an insulating material. In the present method, both a photo-sensitizer, which is able to oxidize pyrrole, and a sacrificial oxidant which is not able to oxidize pyrrole directly, are required for the present system. It was demonstrated that photo-sensitized polymerization proceeded following the oxidation of pyrrole by photo-excited $Ru(bpy)_3^{3+}$ through the oxidative electron transfer process. The mechanism is illustrated in Figure 7. In this experiment, a cation-exchange membrane (Nafion) was used for the polymer matrix to achieve a smooth reaction, as the membrane acts as a dopant of the resulting polypyrrole.

The photopolymerization was carried out through a photomask under irradiation from a dye laser (490nm). The fine and red conducting polypyrrole pattern was formed on an organic membrane such as Nafion, as is shown in Figure 8. The line width is considered to be at sub-micrometer level from the present preliminary study. Three-dimensional patterning is also possible by this method with multi-layers containing different kinds of sensitizer with light of different wavelength. In addition, both wet and dry patterning processes are suggested.

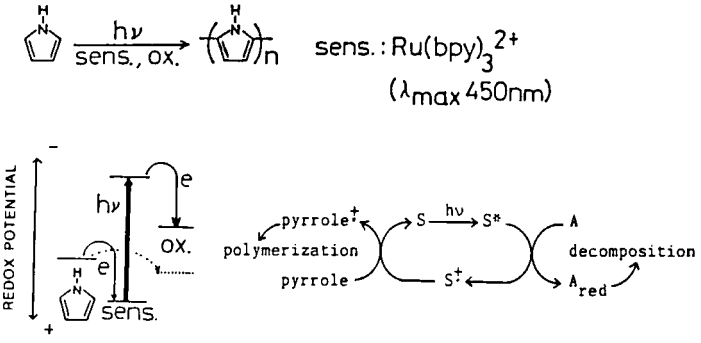


FIGURE 7 Photopolymerization of pyrrole.

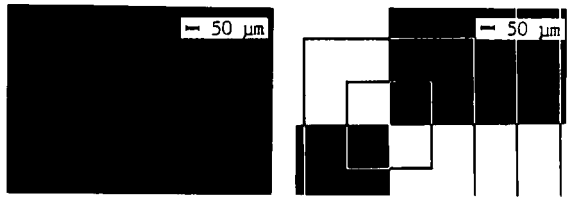


FIGURE 8 Polypyrrole photo-polymerized on a Nafion film (Left) and photo-mask (Right).

3. Multi-mode chemical signal transducer molecule[4,21,22]

It is an important problem to try to build highly integrated transformation modes into one molecule, in order to construct an advanced functional molecular device. Here, a new class of chemical transducer is demonstrated. This has a plurality of transformation modes via independent stimulations, as a result of which response by one stimulation can be regulated by another stimulation. Consequently, a molecule with n responsive regions would have 2^n states corresponding to n transformation processes by every independent stimulation.

Based the above concept, we have investigated the conjugated transformation of multi-mode chemical transducers. Figure 9 shows 2-(4′-methoxyphenylazo)anthraquinone, which has a photoresponse and a chemical redox response, as an example. This molecule has 4 ($= 2^2$) distinguished states, and plays a significant role as a new chemical transducer in dual modes as electrochromism and photochromism.

The present conjugated function, is to be appreciable for dual-mode memory; one is a deep memory moded in electrochromism and the other is a shallow memory moded in photochromism, or another utilizable function is that the deep memory is moded in hydroquinone-type photochromism hard to be transformed and the shallow memory is moded quinone-type one easy to be transformed. Such multi-mode signal transducer molecules hold the prospect of promoting the functionality of molecular devices.

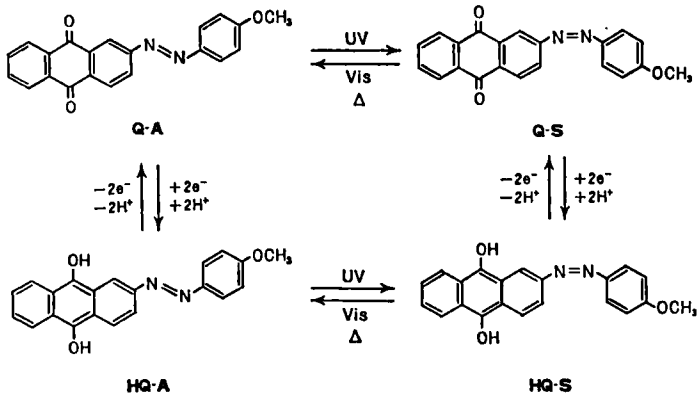


FIGURE 9 A dual mode transducer molecule responsive to redox- and photo-stimulations.

References

1. T. Shimidzu, *Reactive Polymers*, **6**, 221–227 (1987).
2. T. Iyoda, A. Ohtani, T. Shimidzu and K. Honda, *Synthetic Metals*, **18**, 725–730 (1987).
3. T. Shimidzu, T. Iyoda, A. Ohtani, M. Ando and K. Honda, *Molecular Electronic Devices*, 599–608 (1988).
4. T. Shimidzu, *Reactive Polymers*, **11**, 177–189 (1989).
5. T. Shimidzu, A. Ohtani, M. Aiba and K. Honda, *J. Chem. Soc., Faraday Trans.*, **84**, 3941–3949 (1988).
6. T. Shimidzu, A. Ohtani, T. Iyoda and K. Honda, *J. Chem. Soc., Chem. Commun.*, 1414–1415 (1986).
7. T. Iyoda, T. Ohtani, T. Shimidzu and K. Honda, *Chem. Lett.*, 687–690 (1986).
8. idem, *Synthetic Metals*, 747–751 (1986).
9. T. Shimidzu, A. Ohtani, T. Iyoda and K. Honda, *J. Electroanal. Chem.*, **224**, 123–135 (1987).
10. T. Shimidzu, A. Ohtani and K. Honda, ibid., **251**, 323–337 (1987).
11. idem, *Bull. Chem. Soc. Japn.*, **61**, 2885–2890 (1988).
12. A. Ohtani and T. Shimidzu, ibid. **62**, 234–238 (1989).
13. T. Shimidzu, A. Ohtani, T. Iyoda and K. Honda, *J. Chem. Soc., Chem. Commun.*, 327–328 (1987).
14. M. Ohtani, M. Abe, H. Higuchi and T. Shimidzu, *Bull. Chem. Soc. Japn.*, **62**, 234–238 (1989).
15. T. Shimidzu, A. Ohtani, T. Iyoda and K. Honda, *J. Chem. Soc., Chem. Commun.*, 1414–1415 (1986).
16. T. Iyoda, M. Ando, T. Kaneko, A. Ohtani, T. Shimidzu and K. Honda, *Tetrahedron Lett.*, **27**, 5633–5636 (1986).
17. ibid., Langmuir, **3**, 1169–1170 (1987).
18. T. Shimidzu, T. Iyoda, M. Ando, A. Ohtani, T. Kaneko and K. Honda, *Thin Solid Films*, **160**, 67–79 (1988).
19. T. Shimidzu, T. Iyoda, H. Segawa, T. Saika and K. Honda, *MRS Int. Adv. Mat.*, **12**, 261–266 (1989).
20. H. Segawa, T. Shimidzu and K. Honda, *J. Chem. Soc., Chem. Commun.*, 132–133 (1989).
21. T. Shimidzu, T. Iyoda and K. Honda, *Pure and Applied Chem.*, **60**, 1025–1032 (1988).
22. T. Iyoda, T. Saika, K. Honda and T. Shimidzu, *Tetrahedron Lett.*, 5429–5432 (1989).