Recent Progress of Electro- and Photo-Functional Polymers and Their Applicaions

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Properties of polymers are strongly dependent on their molecular structures of main chains and substituents in the side chain and also on their morphology. We have studied both insulating polymers with saturated single bonds in the main chains and also functional polymers with highly conjugated structures either in the main chains or in substituted side chains. Functional polymers can also be realized by introduction of large dipole moments or spins in their structures just as liquid crystalline polymers, ferroelectric polymers and ferromagnetic polymers.

Among various such functional polymers, here, I will discuss mainly functional polymers based on conducting polymers whose main chains are composed of highly extended conjugated electron system.

Because of conjugated structures in the main chains, conducting polymers exhibits characteristics as semiconductors and insulators with relatively small band gaps ranging from 0.5eV to 3.5eV depending on their molecular structures. Substituents and hetero-atoms in the molecular structure, planarity of conjugation in the main chain and also strength of inter-chain interaction influence strongly on the band gap. This also means that the desired band gap of material can be designed and tailored. The absolute energy levels in electronic states influence also on the electrical properties. It should also be mentioned that because of those relatively small band gap energies, conducting polymers can interact with infrared, visible and ultraviolet lights. As is well known conducting polymers undergo reversible insulator-metal transition upon doping of various acceptor or donor dopants.

These facts suggest that various functional applications of conducting polymers are possible. Indeed various functional applications of conducting polymers have so far been proposed.

We have also proposed and demonstrated various applications of conducting polymers based on our fundamental studies. Though, among many proposed applications of conducting polymers only several devices such as battery and condenser have been successfully fabricated and sent to market so far, we are convincing that various other functional applications should also be realized in the industrial scale in the near future. It should also be mentioned that by the introduction of functional molecular units in the side chain, the application of conducting polymers should become more promising.

At the first, we will discuss the properties of conducting polymers as function of molecular structures and show that contrary to common sense so far believed anomalous characteristics appear by the modification of molecular structures.

For example, polyacetylenes have been considered to be non-emissive and their characteristics can be explained by soliton model. However, we have demonstrated that in disubstituted polyacetylenes strong photoluminescence (PL) is observed and their emission characteristics such as wavelength of PL and efficiency are dependent on the structures of substituents. For example, intense green PL and blue PL were observed in poly(de-phenylacetylene) (PDPA) and poly(1-alkyl 2-phenylacetylene) (PAPA) and their intensity increases with increasing with increasing alkyl chain length or

by introduction of bulky substituents.

Except for fundamental research we have also studied electroluminescence (EL) in conducting polymers in the device with the structure of cathode/conducting polymer/anode. In most cases as anode ITO was used and as cathode either MgIn alloy or aluminum (Al) were used. We have demonstrated red, green and blue ELs utilizing polythiophene derivatives, poly (p-phenylenevinylene) derivatives and polyfluorene derivatives for examples. We have also show that polyacetylene derivatives PDPA and PAPA also exhibits strong green and blue ELs.

Except for common structure of EL devices, we indicated that polarized EL can be realized utilizing a device fabricated with oriented conducting polymer prepared by quite simple rubbing method.

Color variable EL devices were also demonstrated utilizing multilayered structure of devices, in which emission color depends on the polarity of applied voltage. Electrochemical EL devices were also reported by us.

Highly efficient PL and EL suggest the possibility of lasing in conducting polymers.
We have studied photo-modulation spectroscopy in conducting polymer and revealed photo-induced absorption and stimulated emission in the spectrum.

Dynamics of excitons in conducting polymers have also be studied. In these studied we convinced the possibility of lasing in conducting polymers.

We have demonstrated remarkable spectral narrowing of emission upon optical excitation at relatively low excitation level in various conducting polymers such as poly(2,5-dialkoxyphenylenevinylene)s, PDPA, PAPA and polyfluorene derivaties in films. The observed spectral narrowing are discussed in terms of superradiation, superfluorescence and amplified spontaneous emission.

By forming micro-ring cavity either by covering surface of glass fibers of micron-meter scale in diameter with conducting polymer, laser emission with spectral width less than 1nm and extremely low threshold of optical excitation less than 0.1 nJ/cm2 was demonstrated and explained either by wave-guided mode or gallery whispering mode.

We have also demonstrated cylindrical structure of EL device with Al/conducting polymer/ITO coated fiber.

We found liquid crystalline behavior in poly(2,5-dialkoxyphenylenevinylene) such as poly(2,5-dinonyl oxyphenylenevinylene) whose main chain has rigid structure contrary of conventional polymer liquid crystals with flexible main chains. It should also be mentioned that upon introduction of substituents containing mesogen units in the side chain of poly(p-phenylenevinylene) conducting polymer liquid crystal was realized in which EL was also observed.

Various other functional applications such as new concept of photo-voltaic devices utilizing conducting polymer and C60 and also p-type and n-type conducting polymers have been proposed and their novel characteristics have been demonstrated.

Some of our recent activities in the field of fundamental study and applications of functional polymers such as conducting polymers are included in following recent publication lists.

References

[1] K.Tada, M.Onoda, M.Hirohata, T.Kawai and K.Yoshino "Blue-Green Electroluminescence in Copolymer Based on Poly(1,4-phenyleneethynylene)", Jpn.J.Appl.Phys. 35 (1996) L251-L253

[2] E.Frankevich, A.A.Zakhidov, K.Yoshino, Y. Maruyama and K.Yakushi, "Photoconductivity of poly(2,5-diheptyloxy-p-phenylenevinylene) in the air atmosphere: Magnetic-field effect and mechanism of generation and recombination of charge carriers", Phys. Rev. B 53 (1996) 4498-4508

[3] Hisashi Araki, Anvar A. Zakhidov, Kazuya Tada, Kyuya Yakushi and Katsumi Yoshino, "Alkali-metal doping of fullerene-conducting polymer composite: evolution of conductivity and ESR", Synthetic Metals 77 (1996) 291-297

[4] A.A.Zakhidov, H.Araki, K.Tada, K.Yoshino, "Fullerene-conducting polymer composites: intrinsic charge transfer processes and doping effects",Synthetic Metals 77 (1996) 127- 137

[5] Tsuyoshi Kawai, Takahiro Yamaue, Kazuya Tada, Mitsuyoshi Onoda, Sung-Ho Jin, Sam-Kwon Choi and Katsumi Yoshino, "Fabrication of Multilayered Conducting Polymer Heterostructure by Self-Assembly Technique and Its Optical and Electrical Properties", Jpn.J.Appl.Phys. Vol.35(1996) L741-L744

[6] Maki Hamaguchi, Hideo Sawada, Jun Kyokane and Katsumi Yoshino, "Blue Electro-luminescence from Poly(p-phenylene) Solubilized by Perfluorpropylation", Chemistry Letters 1996 527-528

[7] Kazuya TADA, Hiroshi HARADA and Katsumi YOSHINO,"Polymeric Bipolar Thin-Film Transistor Utilizing Conducting Polymer Containing Electron Transport Dye", Jpn. J.Appl.Phys. Vol. 35(1996)L944-L946

[8] Akihiko FUJII, Kenji YOSHIMOTO, Masayoshi YOSHIDA, Yutaka OHMORI, Katsumi YOHINO, Hideki UENO, Masaya KAKIMOTO and Hiroyoshi KOJIMA, "Electroluminescent Diodes Utilizing Polysilanes", Jpn.J.Appl.Phys. Vol.35(1996) 3914-3917

[9] Katsumi YOSHINO, Kentaro KOBAYASHI, Katsunori MYOJIN, Masanori OZAKI, Kazuo AKAGI, Hiromasa GOTO and Hideki SHIRAKAWA," Liquid Crystalline Behaviors of Conducting Polyacetylene Derivative with Mesogenic Substituent and Its Mixture with Ferroelectric Liquid Crystal", Jpn.J.Appl.Phys. Vol.35(1996) 3964-3970

[10] Maki Hamaguchi and Katsumi Yoshino, "Color-variable electroluminescence from multilayer polymer films", Appl.Phys.Lett. 69(1996)143-145

[11] Katsumi Yoshino, Kazuya Tada, Kenji Yoshimoto, Masayoshi Yoshida, Tsuyoshi Kawai, Hisashi Araki, Maki Hamaguchi, Anvar Zakhidov, "Electrical and optical properties of molecularly doped conducting polymers", Synthetic Metals 78(1996) 301-312

[12] Katsumi Yoshino, Anvar A. Zakhidov, Hirotake Kajii, Hisashi Araki, Kazuya Tada, Takanobu Noguchi, Toshihiro Ohnishi, Kyuya Yakushi, "Multiphase superconductivity in OO-PPV/C60 composite doped by alkali metals Low-field microwave absorption and SQUID study", Physica 264 (1996) 161-171

[13] Kazuya TADA, Rahmat HIDAYAT, Masaharu HIROHATA, Masahiro TERAGUCHI, Toshio MASUDA and Katsumi YOSHINO, "Optical Properties and Blue and Green Electro-luminescence in Soluble Disubstituted Acetylene Polymers", Jpn.J.Appl.Phys. Vol.35 (1996)L1138-L1141

[14] Masaharu FUJII, Takenori IZAWA, Hideomi OHNISHI, Kiyomitsu ARII and Katsumi YOSHINO, "Neuron-Type Conducting Polymers Prepared Electrochemically and Their Connection", Jpn.J.Appl.Phys. Vol. 35(1996) 290-293

[15] Maki HAMAGUCHI and Katsumi YOSHINO, "Color-Variable Emission in Multilayer Polymer Electroluminescent Devices Containing Electron-Blocking Layer", Jpn.J. Appl. Phys. Vol.35(1996)4813-4818

[16] Xiao Hong YIN, Katsumi YOSHINO, Hideo YAMAMOTO, Toshiro WATANUKI, Isao ISA, Shinichi NAKAGAWA and Mikio ADACHI, "Electrical Conduction near Percolation Threshold in Polymer Composite Containing Conducting Polypyrrole-Coated Insulating Polymer Fiber", Jpn.J.Appl.Phys. Vol.35 (1996)4692-4695

[17] Sergey V.FROLOV, Masanori OZAKI, Werner GELLERMANN, Zeev V. VARDENY and Katsumi YOSHINO, "Mirrorless Lasing in Conducting Polymer poly(2,5-dioctyloxy-p-phenylenevinylene)Films", Jpn.J.Appl.Phys. Vol.35(1996)L1371-L1373

[18] P.A.Lane and J.Shinar K.Yoshino, "Photo-luminescence-detected magnetic-resonance study of fullerene-doped Pi-conjugated polymers", PHYSICAL REVIEW B 54 (1996) 9308-9313

[19] Akihiko FUJII, Anvar A. ZAKHIDOV, Victor V. BOROVKOV, Yutaka OHMORI and Katsumi YOSHNO, "Organic Photovoltanic

Cell with Donor-Acceptor Double Hetero-junctions", Jpn.J.Appl.Phys. Vol. (1996)L 1438-L1441

[20] Maki HAMAGUCHI, Akihiko FUJII, Yutaka OHMORI and Katsumi YOSHINO, "Voltage-and Polarity-Tunable Multicolor Organic Electroluminescent Devices", Jpn.J.Appl.Phys. Vol.35(1996)L1462-L1464

[21] K.Yoshino, X.H.Yin, K.Tada, T.Kawai, M.Hamaguchi, H.Araki, R.Sugimoto, N. Uchikawa, T.Asanuma, M.Kawahigashi and H.Kato, "Novel Properties of New Type Conducting and Insulating Polymers and their Composites", IEEE Transaction on Dielectrics and Electrical Insulation 3(1996) 331-344

[22] Hideo Yamamoto, Masashi Oshima, Minoru Fukuda, Isao Isa, Katsumi Yoshino, "Characteristics of aluminum solid electrolytic capacitors using a conducting polymer", Journal of Power Sources 60 (1996) 173-177

[23] Maki HAMAGUCHI, Hidetaka NAMBU and Katsumi YOSHINO, "Electrogenerated Chemiluminescence from Poly(3-hexylthiophene)",Jpn. J.Appl.Phys. Vol.36(1997)L124-L126

[24] M.Chandross, S.Mazumdar, M.Liess, P.A.Lane, Z.V.Vardeny, M.Hamaguchi and K.Yoshino, "Optical absorption in the substituted phenylene-based conjugated polymers:Theory and experiment", PHYSICAL REVIEW B 55(1997) 1486~1496

[25] Xiao Hong YIN, Katsumi YOSHINO, Kenichi HASHIZUME and Isao ISA," Preparation and Electrical Properties of Conducting Polyaniline-Polycarbonate Composite Films", Jpn.J.Appl.Phys. 36(1997) 3537-3540

[26] Rahmat HIDAYAT, Masaharu Hirohata, Masahiro Teraguchi, Toshio Masuda and Katsumi Yoshino, "Effect of Molecular Structure of Substitutes on Green Electroluminescence in Disubstituted Acetylene Polymers", Jpn.J.Appl.Phys.36 (1997) 3746-3743

[27] Kohji Tashiro, Masamichi Kobayashi, Tsuyoshi Kawai and Katsumi Yoshino, "Crystal structural change in poly (3-alkyl thiophene)s induced by iodine doping as studied by an organized combination of X-ray diffraction, infrared/Raman spectroscopy and computer simulation techniques", Polymer 38(1997)2867-2879

[28] Maki HAMAGUCHI, Hidetaka NAMBU, Toshiyuki OHSAWA, and Katsumi YOSHINO, "A Comparative Study Of D-C Electrochemiluminescence from Poly (2-methoxy-5-dodecyloxy-p-pheynylenevinylene) in solution and in Solid Polymer Electrolyte Media", Jpn.J.Appl.Phys. 36 (1997) L679-L6

[29] Katsumi YOSHINO and Ray HBAUGHMAN, "The Optical Properties of Porous Opal Crystals Infiltrated with Organic Molecules", Jpn.J.Appl.Phys. 36(1997) L714-L717

[30] Kazuya TADA$B!"(JHiroshi HARADA and Katsumi YOSHINO," Field-Effect Mobility of Molecularly Doped Poly (3-hexylthiophene)", Jpn.J.Appl.Phys. 36(1997) L718-L720

[31] Hirotake Kajii, Hisashi Araki, Anvar. A.Zakhidov, Kazuya Tada, Kyuya Yakushi, Katsumi Yoshino, "Microwave heating effect on two Josephson-junction systems in granular PAT12-C60-Rb composites: low-field microwave absorption study", Physica C 277(1997) 277-284

[32] Katsumi Yoshino, Kazuya Tada, Akihiko Fujii, Esther M. Conwell, and Anvar A. Zakhidov, "Novel Photovoltaic Devices Based on Donor-Acceptor Molecular and Conducting Polymer Systems", IEEE Transactions on electron devices 44 (1997)1315-1324

[33] Maki Hamaguchi and Katsumi Yoshino, "Polarized Fluorescence and Electroluminescence from Rubbingaligned Conjugated Polymers and Their Composites with Fluorescent Dyes", Polymers for Advanced technologies 8(1997)

[34] Sergey V. FROLOV, Maxim SHKUNOV, Z. Valy VARDENY, Kazuya Tada, Rahmat HIDAYAT, Masaharu HIROHATA, Masahiro TERAGUCHI, Toshio MASUDA and Katsumi YOSHINO ,"Spectral Narrowing of Emission in Di-substituted Polyacetylene", Jpn. J. Appl. Phys. 36 (1997)

L1268-L1271

[35] Kazuya TADA and Katsumi YOSHINO, "Conducting Polymer Color Sensor", Jpn. J. Appl. Phys. 36 (1997) L1351-L1353

[36] Mitsuyoshi ONODA, Hiroshi NAKAYAMA, Takahiro YAMAUE, Kazuya TADA and Katsumi YOSHINO, "Properties of Light-Emitting Diodes Fabricated from Self-Assembled Multilayer Heterostructures of Poly (p-pyridyl vinylene)", Jpn. J. Appl. Phys. 36 (1997) 5322-5328

[37] Anvar.A.Zakhidov and Katsumi Yoshino, "Strategies for improving molecular donor-acceptor photocells: Selective doping and excitonic layers", Synthetic Metals 85 (1997) 1299-1302

[38] S.V.Frolov, M.Liess, P.A.Lane, W.Gellermann, Z.V.Vardeny, M.Ozaki and K.Yoshino, "Exciton Dynamics in soluble Poly (p-Phenylene-vinylene): Towards an Ultrafast Excitonic Switch", PHYSICAL REVIEW LETTERS 78(1997) 4285-4288

[39] M.Ozaki, E. Ehrenfreund, R.E,Benner, T. J.Barton, K.Yoshino and Z.V.Vardeny, "Dispersion of Resonant Raman Scattering in (Pi-Conjugated Polymers: Role of the Even Parity Excitons", PHYSICAL REVIEW LETTERS 79(1997) 1762-1765

[40] S.V.Frolov, M.Shkunov, Z.V.Vardeny, and K.Yoshino,"Ring microlasers from conducting polymers", PHYSICAL REVIEW B 56(1997) R4363-R4366

[41] Hidetake Nambu, Maki Hamaguchi, Katsumi Yoshino, "A Comparative study of electro-generated chemiluminescence in poly (3-hexylthiophene) and poly (2-methoxy -5-p-phenylenevinylene)", J.Appl.Phys.82 (1997) 1847-1852

[42] Kazuya Tada, Mitsuyoshi Onoda and Katsumi Yoshino, "Optical properties and electronic structure of poly (1,4-bis(2-thienyl)-2,5-dialkoxyphenylene)", J. Phys.D: Appl.Phys. 30 (1997) 2063-2068

[43] Katsumi YOSHINO Kazuya TADA, Masaharu HIROHATA, Rahmat HIDAYAT, Satoshi TATSUHARA, Masanori OZAKI and Mitsuo ISHIKAWA, "Emission Characteristics of Poly [(tetraalkyldisilanylene)-p-oligophenylene]s", Jpn.J.Appl.Phys.36 (1997) L1548-L1551

[44] M.Liess, S.Jeglinski, Z.V.Vardeny, M.Ozaki, K. Yoshino Y.Ding and T.Barton, "Electro-absorption spectroscopy of luminescent and nonluminescent Pi-conjugated polymers", PHYSICAL REVIEW LETTERS B 56(1997) 712-724

[45] Kazuya TADA, Yoshihiro YOKOTA, Koji KOBAYASHI and Katsumi YOSHINO, "Characteristics of Heterojunction Utilizing Conducting Polymer and Diamond Film on Si", Jpn.J.Appl.Phys 36(1997) L1678-L1680

[46] M.Liess, S.Jeglinski, Z.V.Vardeny M.Ozaki, K.Yoshino, Y.Ding and T.Barton, "Electro-absorption spectroscopy of luminescent and nonluminescent Pi-conjugated polymers", PHYSICAL REVIEW B 56(1997) 712-724

[47] Rahmat HIDAYAT, Masaharu HIROHATA, Kazuya TADA, Masahiro TERAGUCHI, Toshio MASUDA and Katsumi YOSHINO, " Photoluminescence and Electroluminescence in Polymer Mixture of Poly(alkylphenylacetylene) and Poly(diphenylacetylene) Derivatives", Jpn.J.Appl.Phys 37(1998) L180-L183

[48] Segey Lee, Joon Y. Park, Young S. Park, Yung W. Park, Yuliang Li, Daoben Zhu, Kazuya Tada, Tsuyoshi Kawai and Katsumi Yoshino, "PHOTOPHYSICAL PROPERTIES OF A NEW C60-DERIVATIVE AND ITS COMPOSITE WITH POLY (3-DODECYL-THIOPHENE)", Solid State Communications 105(1998) 345-349

[49] S.V.Frolov,P.A.Lane,M.Ozaki,K.Yoshino and Z.V.Z.V.Vardeny," Picosecond to milisecond photoexcitation dynamics in blends of C60 with poly(pphenylene vinylene) polymers", Chem.Phys.Letters 286(1988)21-27

[50] S.V.Frolov, Z.V.Vardeny and K.Yoshino, "Cooperative and stimulated emission in poly(p-phenylene-vinylene) thin films and solutions", Physical Review B 57(1988) 9141-9147

[51] S.Frolov, Z.V.Vardeny and K.Yoshino, "Plastic microring lasers on fibers and wires", Appl.Phys.Letters 72(1988)1802