Photoluminescence characterization of polythiophene films incorporated with highly functional molecules such as metallophthalocyanine

Hiroaki Kobe, Kazumasa Ohnaka, Hitoshi Kato,^{a)} Susumu Takemura, Kazuhiro Shimada, and Tomoyasu Hiramatsu

Department of Electrical, Electronic and Information Engineering, College of Engineering, Kanto Gakuin University, 1-50-1 Mutsuuraigashi, Kanazawa-ku, Yokohama 236-8501, Japan

Kazunori Matsui

Department of Material and Life Science, College of Engineering, Kanto Gakuin University, 1-50-1 Mutsuuraigashi, Kanazawa-ku, Yokohama 236-8501, Japan

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The photoluminescence (PL) of conducting polymer polythiophene (PT) films incorporated with metallophthalocyanines (PcMs) such as CuPc, MgPc, FePc, Li₂Pc, and CoPc was studied by PL and time-correlated single photon counting (TCSPC) measurements. Polymer films were prepared by electrochemical polymerization and PcMs migrated into the polymer films by a diffusion method using acetonitrile or toluene as a solvent to dissolve the PcMs. The wavelength of PL emission peaks changed significantly depending on the solvent used in the doping process. Using acetonitrile, the observed PL emission peaks originated from the Q band, whereas they were assigned to the Soret band in the case of toluene. TCSPC measurements showed that PL emission took place through a ligand–ligand transition process when using acetonitrile because the average lifetimes were comparable and independent of the central metal ions for CoPc-, Li₂Pc-, and MgPc-doped polymer films. Conversely, using toluene, it was found that ligand–ligand emission occurred for Li₂Pc-, MgPc-, and FePc-doped films. To identify the cause of the drastic change in PL emission pattern, x-ray photoelectron spectroscopy measurements were obtained. A lower binding energy component appeared in the C 1s core-level spectra of acetonitrile-processed PcM-doped PT films, whereas this component shifted to higher energy and overlapped with the main peak for toluene-processed PcM-doped PT films. The lower binding energy component corresponded to photoelectrons due to the C atoms in the benzene rings of the ligand. Lower binding energy components also appeared in the N 1s core-level spectra of acetonitrile-processed PcM-doped PT films, and this component shifted to higher energy for toluene-processed PcM-doped PT films. These lower energy components were assigned to the core-level peaks due to the N atoms at the meso position bridging between pyrrole rings. This suggests that the electron charge at the N sites of the meso positions in toluene-processed films was smaller than in acetonitrile-processed ones. The changes in energy at benzene C sites and meso N sites suggest that the electronic states of the phthalocyanine in the toluene-processed films were porphyrin-like, so the Soret band became dominant in the PL emission spectrum. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4772946>]

I. INTRODUCTION

The development of hybrid organic materials^{1–5} is important not only to improve the fundamental understanding of electrical and optical properties but also to realize molecular organic devices. The aim of this study is to develop a hybrid material combining highly functional molecule metallophthalocyanine (PcMs) and conducting polymer polythiophene (PT)⁶ for use in electronic and optical devices. PcMs are colorful materials that possess high thermal stability and show fast colors. They are also unreactive to acids and alkalis. PcMs complexes exhibit strong optical absorption in the visible range and favorable electrical properties.^{7–9} PcMs are highly conjugated π -electron structures and are attractive synthetic materials because the diversity of their structures and unique optical and electrical properties lead to wide

range of potential applications such as photovoltaic cells,^{10–13} nonlinear optics,¹⁴ photoconducting materials,¹⁵ electrochromic substances,^{16,17} Langmuir–Blodgett films,¹⁸ and carrier generation materials in the near infrared region.¹⁹

The present study focuses on the photoluminescence (PL) properties of PcMs doped in PT to investigate how PcMs affect the emission properties of PT and what the cause of the changes in the PL properties is when PcM molecules are injected into the polymer matrix through a doping process. The optical properties of the isolated phthalocyanine molecules dispersed in solution have been observed by PL measurements.^{20–23} Phthalocyanine exhibits an intense absorption spectrum from 500 to 700 nm originating from the Q band.²⁴ The absorption spectrum of phthalocyanine differs significantly from that of porphyrin, which exhibits intense peaks from 400 to 500 nm corresponding to the Soret band and weak Q band peaks.^{25,26} Although the structure of phthalocyanine is similar to that of porphyrin, there are two major

^{a)}Electronic mail: hkato@kanto-gakuin.ac.jp

structural differences. One is the presence of benzene rings in the phthalocyanine ligand. The other is the different elements at the meso positions. Phthalocyanine and porphyrin possess N and C atoms, respectively, at their meso positions. The difference in the absorption spectra between porphyrin and phthalocyanine has been theoretically explained based on the molecular orbitals at the meso positions bridging between the pyrrole rings and at the C sites of the ligand benzene rings.²⁷ The difference in electron densities at the meso-positions and at the C-sites of benzene rings between phthalocyanine and porphyrin changes their excited states, which leads to a drastic shift of absorption spectrum.

In the present study, the PL properties of conducting polymer PT films doped with PcMs such as CuPc, MgPc, FePc, Li₂Pc, and CoPc were studied comprehensively by PL and time-correlated single photon counting (TCSPC)^{28–32} measurements to determine the fundamental PL properties of various PT-phthalocyanine complexes prepared using different solvents. Polymer films are prepared by electrochemical polymerization. PcMs are doped into the polymer films using a diffusion method with acetonitrile or toluene as a solvent, whereby the dopant species dissolved in the solvent migrate into the polymer films. The dependence of PL properties and emission states on the PcMs in the conducting polymer is determined. X-ray photoelectron spectroscopy (XPS) measurements are also conducted to clarify the origin of PL and investigate the cause of the PL behavior.

II. EXPERIMENT

PT used in the present study was an electrochemically synthesized α - α' -linked polymer that was polymerized from thiophene with no alkyl side chains. PT films were electrochemically synthesized on indium tin oxide (ITO) substrates with a resistivity of 30 Ω/cm^2 in an electrochemical cell using a voltage-controlled method. Electrochemical polymerization was performed in acetonitrile containing thiophene monomer (0.05 M) and tetraethylammonium tetrafluoroborate (0.1 M) as a supporting electrolyte under a N₂ atmosphere. The ITO substrate was used as a working electrode (anode) for polymerization. Platinum mesh and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrochemical cell was controlled using a potentiostat (HZ-5000 HAG3100, Hokuto Denko Co, Ltd.). Typically, a voltage of 3.5 V versus the reference electrode was applied to the anode for 300 s to synthesize the PT films. BF₄[−] anions were doped in the as-grown films. Injection of PcMs into the PT films was performed by a diffusion method. PcMs were diffused into the PT films by dipping the as-grown PT films in saturated solutions of each PcM in acetonitrile or toluene.

PL measurements were obtained on a fluorescence spectrometer (Horiba Fluorolog-3). PL emission peaks were discriminated from Stokes and anti-Stokes scattering peaks by changing the excitation wavelength from 300 to 440 nm. TCSPC lifetime measurements were also conducted on a fluorescence spectrometer (Horiba Fluorolog-3). In the TCSPC system, the decay curve was obtained by plotting detected

single photon counts excited by a 371 nm laser pulse for each detection time channel. Each time channel corresponded to 1.97 ns, and the total measurement time was 1000 channels. The intrinsic decay curve of emitted photons from each decay component was obtained by fitting exponential lifetime decay components including an instrument function with deconvoluting the original decay curve. The fitting calculation yielded component lifetime values and corresponding relative amplitudes. The relative amplitude is the probability of photon emission from each decay component. Average lifetime values of decay components were calculated from each lifetime multiplied by its relative amplitude.

XPS measurements were conducted under an ultrahigh vacuum of 10^{−8} Pa using an XPS (ESCA AXIS ULTRA DLD, Kratos Co. Ltd.). Monochromatic Al K α was used as an x-ray source. A pass energy of 40 eV was used. XPS spectra were fitted by Gaussian-Lorentzian functions with a ratio of 70%/30%.

III. RESULTS AND DISCUSSION

A. PL and lifetime measurements

Clear differences in the emission patterns between acetonitrile- and toluene-processed PT-PcM films were observed in PL measurements. When acetonitrile was used as the solvent in the doping process, the observed emission peaks were dominated by the Q band. In contrast, using toluene as a solvent caused the Soret band to dominate.

Remarkably similar changes occurred in the emission patterns for Li₂Pc- and MgPc-doped PT films prepared using different solvents with respect to absorption and emission states. Both dopants include central metal ions without d-electrons. In the case of Li₂Pc-doped films prepared using acetonitrile as a solvent in the doping process, two intense emission peaks were observed at 600 and 660 nm, as shown in Fig. 1(b). The corresponding absorption peaks were observed at 445 and 465 nm [Fig. 1(a)]. In the case of a toluene-processed Li₂Pc-doped film, strong emission peaks were observed at 445 and 482 nm in the Soret band region, as illustrated in Fig. 1(d). Figure 1(c) shows the corresponding absorption peak at 295 nm. In the case of MgPc-doped films, the same characteristic change in pattern was observed. The absorption and PL spectra of MgPc-doped PT films are illustrated in Fig. 2. For the film processed in acetonitrile, the absorption peaks were observed at 445 and 465 nm [Fig. 2(a)] like those of Li₂Pc-doped PT. In the PL spectrum, a single weak emission peak was observed at 663 nm in the Q-band region, as shown in Fig. 2(b). The intensity of the Q-band differed between Li₂Pc- and MgPc-doped PT films. In the case of a toluene-processed PT film, strong emission peaks appeared at 455 and 485 nm in the Soret band region [Fig. 2(d)]. Figure 2(c) shows the corresponding absorption peak at 320 nm, which was almost the same as that of Li₂Pc-doped PT film.

The CoPc-, FePc-, and CuPc-doped samples exhibited PL spectra with different emission peak profiles compared to those of Li₂Pc- and MgPc-doped samples, although the PL

FIG. 1. (Color online) Photoluminescence absorption and emission spectra of PT films incorporated with Li_2Pc by a diffusion method using acetonitrile or toluene as a solvent. (a) Absorption spectrum (solvent: acetonitrile). (b) Emission spectrum (excitation wave length: 440 nm; solvent: acetonitrile). (c) Absorption spectrum (solvent: toluene). (d) Emission spectrum (excitation wave length: 320 nm; solvent: toluene).

pattern change follows the rule basically. CoPc, FePc, and CuPc contain central ions with d-electrons. The PL and absorption spectra of CoPc-doped PT films are illustrated in Fig. 3. In the case of the film processed in acetonitrile, a weak emission peak was observed at 665 nm in the Q-band region [Fig. 3(b)]. The corresponding absorption peak was observed at 390 nm, as presented in Fig. 3(a), which was at shorter wavelength than those of Li_2Pc - and MgPc -doped PT films. Conversely, for a toluene-processed CoPc-doped PT film, an intense single emission peak appeared at 440 nm in the Soret band region [Fig. 3(d)]. The corresponding absorption peak was observed at 370 nm [Fig. 3(c)], which was at longer wavelength than those of Li_2Pc - and MgPc -doped PT films. Although the change in emission pattern for different

solvents also occurred in the FePc-doped PT film, the PL and absorption spectra (Fig. 4) exhibited different peak profiles than those of the CoPc-doped samples. In the case of the film processed in acetonitrile, absorption peaks were observed at 315, 465, and 480 nm [Fig. 4(c)]. In the PL spectrum, a single Soret band and two Q band emission peaks of medium intensity were observed at 485, 600, and 664 nm, respectively, as depicted in Fig. 4(b). For FePc-doped PT film processed in toluene, a single strong emission peak appeared at 395 nm in the Soret band region [Fig. 4(d)]. The corresponding absorption peak was observed at 325 nm, as shown in Fig. 4(c).

The absorption and PL spectra of CuPc-doped PT films are illustrated in Fig. 5. PL spectra exhibited similar

FIG. 2. (Color online) Photoluminescence absorption and emission spectra of PT films incorporated with MgPc by a diffusion method using acetonitrile or toluene as a solvent. (a) Absorption spectrum (solvent: acetonitrile). (b) Emission spectrum (excitation wave length: 420 nm; solvent: acetonitrile). (c) Absorption spectrum (solvent: toluene). (d) Emission spectrum (excitation wave length: 340 nm; solvent: toluene).

FIG. 3. (Color online) Photoluminescence absorption and emission spectra of PT films incorporated with CoPc by a diffusion method using acetonitrile or toluene as a solvent. (a) Absorption spectrum (solvent: acetonitrile). (b) Emission spectrum (excitation wave length: 400 nm; solvent: acetonitrile). (c) Absorption spectrum (solvent: toluene). (d) Emission spectrum (excitation wave length: 340 nm; solvent: toluene).

emission peak profiles to Li_2Pc - and MgPc -doped samples, although the PL intensity changed. For a CuPc -doped film processed in acetonitrile, a Q band emission peak was observed at 670 nm, as shown in Fig. 5(b). The correspond-

ing absorption peaks were observed at 445 and 465 nm [Fig. 5(a)]. In the case of the film processed in toluene, an intense emission peak appeared at 450 nm was consistent with the Soret band, as presented in Fig. 5(d). The

FIG. 4. (Color online) Photoluminescence absorption and emission spectra of PT films incorporated with FePc by a diffusion method using acetonitrile or toluene as a solvent. (a) and (c) Absorption spectrum (solvent: acetonitrile). (b) Emission spectrum (excitation wave length: 320 nm) (solvent: acetonitrile). (d) Emission spectrum (excitation wave length: 420 nm; solvent: acetonitrile). (e) Absorption spectrum (solvent: toluene). (f) Emission spectrum (excitation wave length: 320 nm; solvent: toluene).

FIG. 5. (Color online) Photoluminescence absorption and emission spectra of PT films incorporated with CuPc by a diffusion method using acetonitrile or toluene as a solvent. (a) Absorption spectrum (solvent: acetonitrile). (b) Emission spectrum (excitation wave length: 400 nm; solvent: acetonitrile). (c) Absorption spectrum (solvent: toluene). (d) Emission spectrum (excitation wave length: 340 nm; solvent: toluene).

corresponding absorption peak was observed at 290 nm [Fig. 5(c)].

To better compare the effect of solvent on PL emission, PL emission measurements for PcM-doped PT films fabricated in acetonitrile and toluene are presented in Tables I and II, respectively. An obvious change in emission pattern between Q and Soret bands, which depends on the solvent used in the doping process, was observed in all of the PcM-doped PT films. The Li_2Pc - and MgPc -doped PT films belong to the same category because the absorption peaks that correspond to the PL emission are the same. However, the PL intensity of the MgPc doped film processed in acetonitrile is weaker than that of the Li_2Pc -doped PT film. The most obvious change in emission pattern was found for Li_2Pc -doped PT films, because intense emission peaks related to Q and Soret bands were observed for the films processed in acetonitrile and toluene, respectively. CoPc - and FePc -doped films with central metal ions containing d-electrons exhibited PL and absorption spectra with different emission peak profiles compared to those of Li_2Pc - and MgPc -doped films. In these films, the absorption peaks corresponding to the PL emissions exhibited different profiles. CuPc -doped PT films processed in different solvents showed minor differences in PL emission, and absorption spectra were the same as those of Li_2Pc - and MgPc -doped PT films.

The above results can be rationalized by considering the theory behind the PL properties of single isolated phthalocyanine and porphyrin molecules.²¹

In porphyrin, the PL emission takes place through intra transition process from the lowest energy singlet excited state to a singlet ground state. According to this theory, the lowest unoccupied molecular orbitals (LUMOs) of porphyrin, e_{gx} and e_{gy} , are degenerate. Because of the low electron density at C sites of meso positions, highest occupied molecular orbital (HOMO) a_{1u} and HOMO-1 a_{2u} are also degenerate. The lowest energy excited states S_1 and S_2 are a hybridization of e_{gx} , e_{gy} , a_{1u} , and a_{2u} . If S_0 denotes a singlet ground state, Q band emission corresponds to the S_1 - S_0 transition and Soret band emission corresponds to the S_2 - S_0 transition. The Soret band dominates as the transition dipole moment $|\langle S_2 | \mathbf{r} | S_0 \rangle|^2$ is small because of the energy degeneracy of a_{1u} and a_{2u} . In contrast, in the case of phthalocyanine, although LUMO e_{gx} and e_{gy} are degenerate, HOMO a_{1u} and HOMO-1 a_{2u} are not degenerate because of the larger electron density at the N sites of the meso positions. Furthermore, the molecular orbitals possess nodes at the C sites of benzene rings linked to the ligand. The lowest energy excited states S_1 and S_2 are a hybridization of e_{gx} , e_{gy} , a_{1u} , and a_{2u} . Denoting the transition dipole moments corresponding to transitions S_0 - S_1 and S_0 - S_2 as $|\langle S_1 | \mathbf{r} | S_0 \rangle|^2$ and $|\langle S_2 | \mathbf{r} | S_0 \rangle|^2$, respectively, their values become comparable because of the energy discrepancy between a_{1u} and a_{2u} . Thus, emissions related to both Q and Soret bands are observed in phthalocyanine. Overall, this means that the electronic states at the N sites of the meso

TABLE I. Photoluminescence emission peaks of PT films incorporated with PcMs by a diffusion method using acetonitrile as a solvent.

		CuPc	MgPc	FePc	Li_2Pc	CoPc
Emission peak (nm)	Soret band	—	—	485	—	—
	Q band	670	663	600	600	665
				664	660	

TABLE II. Photoluminescence emission peaks of PT films incorporated with PcMs by a diffusion method using toluene as a solvent.

		CuPc	MgPc	FePc	Li_2Pc	CoPc
Emission peak (nm)	Soret band	450	455	395	445	440
			485		482	
	Q band	—	—	—	—	—

positions and at the C sites of the benzene rings cause the change in emission pattern between Q and Soret bands compared with those of porphyrin. To determine the reason why the emission pattern strongly depends on the choice of solvent when preparing PcM-doped PT films, N sites at the meso position and C sites of the benzene rings should be investigated by XPS measurements. The results of these measurements are presented in Sec. III B.

To characterize the emission properties of these PcM-doped PT films more fully, emission lifetimes were measured. The results of TCSPC measurements for acetonitrile- and toluene-processed PcM-doped PT films are presented in Tables III and IV. TCSPC decay curves for these films processed in acetonitrile and toluene are illustrated in Figs. 6 and 7, respectively. In the TCSPC measurements, the number of lifetime components fitted to each decay curve ranged between 3 and 5, and lifetimes ranged from several to several hundred nanoseconds. The lifetime and number of components depended not only on the central metal ions of the doped phthalocyanine, but also on the solvent used in the doping process.

Acetonitrile-processed Li₂Pc-, MgPc-, and CoPc-doped PT films are classified into the same group with respect to their emission lifetimes. The decay curve of each compound was composed of three lifetime components with corresponding relative amplitudes, as presented in Table III. The calculated average lifetime for these three compounds was almost the same, around 140 ns. Because both lifetime and the relative amplitude of each decay component were comparable for these three films, it was suggested that emission involved a singlet-singlet transition via an intraligand transition process. In this case, emissions were independent of the

TABLE IV. PL lifetimes of photoluminescence emission of PT films incorporated with PcMs by a diffusion method using toluene as a solvent measured by TCSPC.

Metallophthalocyanine	Components	Lifetime (ns)	Relative amplitude (%)	Average lifetime (ns)
CoPc	1	533.3	17.19	167.9
	2	136.9	40.95	
	3	54.2	35.26	
	4	17.6	6.5	
	5	2.1	0.11	
Li ₂ Pc	1	319.7	28.39	144.4
	2	87.8	56.62	
	3	26.5	14.89	
MgPc	1	349.3	27.24	150.1
	2	88.1	57.87	
	3	26.5	14.89	
CuPc	1	353.9	27.11	151.8
	2	89.2	58.52	
	3	25.7	14.37	
FePc	1	323.3	29.09	146.8
	2	86.3	56.74	
	3	26.6	14.17	

central metal ion in the phthalocyanine complex and were not influenced by spin arising from the d-electrons of metal ions such as Co. The FePc-doped PT sample exhibited a different lifetime profile, with a longer averaged lifetime of 194.3 ns, which was extended because of a long lived component of 673.1 ns. In this case, the emission was supposed to be influenced by a spin effect related to the central Fe ion. The emission involved a singlet-singlet transition mixed with a singlet-triplet transition, which prolonged the lifetime because of a mixture of fluorescence and phosphorescence.

TABLE III. PL lifetimes of photoluminescence emission of PT films incorporated with PcMs by a diffusion method using acetonitrile as a solvent measured by TCSPC.

Metallophthalocyanine	Components	Lifetime (ns)	Relative amplitude (%)	Average lifetime (ns)
CoPc	1	352.7	25.59	148.1
	2	93.9	55.9	
	3	28.8	18.51	
Li ₂ Pc	1	370.5	24.12	149.2
	2	95.8	56.68	
	3	29	19.2	
MgPc	1	343.1	26.72	146.6
	2	90.8	53.88	
	3	32	18.74	
	4	5.9	0.67	
CuPc	1	222.1	34.74	117.7
	2	76.4	47.32	
	3	30.3	16.27	
	4	7.62	1.66	
FePc	1	673.1	16	194.3
	2	184.4	25.75	
	3	80.7	42.89	
	4	31.8	13.45	
	5	13.1	1.91

FIG. 6. (Color online) TCSPC decay curves of acetonitrile-processed PT-PcM films. (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, and (e) CuPc-doped PT.

FIG. 7. (Color online) TCSPC decay curves of toluene-processed PT-PcM films. (a) Li_2Pc -, (b) MgPc -, (c) CoPc -, (d) FePc -, and (e) CuPc -doped PT.

The CuPc -doped PT film exhibited a different lifetime profile, with a short average lifetime of 117.9 ns arising from relatively short lifetime components of 221.4 and 76.1 ns. In this case, the emission was partially influenced by the d-electrons of Cu.

In the case of toluene-processed films, Li_2Pc -, MgPc -, and FePc -doped PT films can be categorized into the same group with respect to emission lifetimes. The decay curve of each compound was composed of three components with corresponding relative amplitudes, as shown in Table IV. In addition, calculated average lifetimes of each compound were similar at around 140 ns. Because both lifetime and the relative amplitude of each decay component were comparable for these three PcM-doped PT films, this suggests that emission was a singlet-singlet transition involving an intraligand transition process. For the FePc -doped PT film, emission was independent of the spin related to the d-electrons of the central metal ion of PcM. The CoPc -doped PT film exhibited a different lifetime profile, with a long average lifetime of 167.9 ns, which was extended by a long lived component of 533.3 ns. In this case, emission was probably influenced by the spin of d-electrons due to the central Co ion. Emission was assumed to be a singlet-singlet transition mixed with a singlet-triplet transition, which prolonged the lifetime because of a mixture of fluorescence and phosphorescence. The CuPc -doped PT film also exhibited a slightly different lifetime profile, with a longer average life (151.8 ns) than the same film processed in acetonitrile (117.9 ns). In this case, the emission was partially influenced by the d-electrons of Cu.

B. XPS measurements

To understand why significant change in emission pattern occurs between PcM-doped PT films processed in acetonitrile

FIG. 8. (Color online) C 1s core-level spectra of acetonitrile-processed PT-PcM films. (a) Li_2Pc -, (b) MgPc -, (c) CoPc -, (d) FePc -, (e) CuPc -doped PT and (f) as-grown PT.

trile and toluene, N sites at the meso position and C sites of the benzene rings were investigated by XPS. XPS C 1s core-level spectra of acetonitrile-processed PcM-doped PT films are shown in Fig. 8. For the acetonitrile-processed Li_2Pc -doped PT film, the C 1s core-level peak was composed of three basic components due to the C atoms in the polymer PT backbone, ligand benzene rings, and pyrrole rings, as shown in Fig. 8(a). The component of lowest binding energy at 283 eV was assigned to C 1s due to ligand benzene rings.³³ The main peak with the largest intensity observed at 284 eV was attributed to the thiophene rings of the PT backbone. The peak observed at 285–286 eV was assigned to C 1s due to the pyrrole rings of Li_2Pc . The lowest energy component at 283 eV suggested that the electron density at the C sites of the benzene rings in Li_2Pc was the same as in an isolated phthalocyanine molecule, which shows characteristic Q-band dominant emission. Lower binding energy components were also observed in the C 1s spectra of MgPc -, CoPc -, FePc -, and CuPc -doped PT complexes, as shown in Figs. 8(b)–8(e), respectively.

The C 1s core-level spectra of toluene-processed PcM-doped PT films are presented in Fig. 9. For the C 1s core-level spectra of toluene-processed Li_2Pc -doped PT film, a lower binding energy component that appeared at 283 eV in the acetonitrile-processed sample clearly shifted to higher energy by 1 eV, as shown in Fig. 9(a). This peak was assigned to C 1s due to the ligand benzene rings, so its change in position suggested that the electronic state at the C sites of the benzene rings of Li_2Pc differed from that of an isolated phthalocyanine molecule, which influenced PL emission. The change in electronic state of the benzene rings

Fig. 9. (Color online) C 1s core-level spectra of toluene-processed PT-PcM films. (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, (e) CuPc-doped PT and (f) as-grown PT.

of Li₂Pc processed in toluene rather than acetonitrile implies that the doped molecules act similar to porphyrins in their PL emission profiles. Energy shifts of the lower binding energy components were also observed in the C 1s spectra of MgPc-, CoPc-, FePc-, and CuPc-doped PT films, as shown in Figs. 9(b)–9(e), respectively. In these films, the lower energy components shifted toward the main energy component assigned to the PT backbone and were overlapped by it.

XPS N 1s core-level spectra of acetonitrile-processed PcM-doped PT films are illustrated in Fig. 10. For the acetonitrile-processed Li₂Pc-doped PT film, the N 1s core-level spectrum was composed of components due to the N atoms of pyrrole rings and the meso positions bridging between pyrrole rings in Li₂Pc, as shown in Fig. 10(a). A component at lower binding energy of 396 eV was assigned to N 1s due to N atoms at meso positions, and the component at 397 eV was attributed to N 1s due to pyrrole rings.³⁴ The position of the lowest energy component at 396 eV suggested that the electron density at the N sites at meso positions was the same as in an isolated Li₂Pc molecule, which lead to the characteristic Q-band emission. Lower binding energy components were also observed in the N 1s spectra of MgPc-, CoPc-, FePc-, and CuPc-doped PT complexes, which are presented in Figs. 10(b)–10(e), respectively.

N 1s core-level spectra of toluene-processed PcM-doped PT films are shown in Fig. 11. For the toluene-processed Li₂Pc-doped PT film, a lower binding energy component that appeared at 396 eV in the acetonitrile-processed sample clearly shifted to higher energy by 2 eV [Fig. 11(a)]. Because this peak was assigned to N 1s due to N atoms at meso positions, it suggested that the electronic state at the N sites of

Fig. 10. (Color online) N 1s core-level spectra of acetonitrile-processed PT-PcM films. (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, and (e) CuPc-doped PT.

the meso positions of Li₂Pc changed significantly compared to that of an isolated phthalocyanine molecule. The shift to higher binding energy corresponds to a decrease of electron density at the N sites of meso positions similar to the C sites of meso positions in the case of porphyrin, so the molecule

Fig. 11. (Color online) N 1s core-level spectra of toluene-processed PT-PcM films. (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, and (e) CuPc-doped PT.

behaves like porphyrin, which results in Soret band dominant emission. Energy shifts of lower binding energy components were also observed in the N 1s spectra of MgPc-, CoPc-, FePc- and CuPc-doped PT films, which are shown in Figs. 11(b)–11(e), respectively, although the spectral profiles differed from that of the Li₂Pc-doped PT film. Multiple lower energy components of low intensity were observed in MgPc-, CuPc-, and FePc-doped PT films.

To analyze the change of electronic states on the PT polymer backbone, S 2p core-level spectra were measured for acetonitrile- and toluene-processed PcM-doped PT films, which are shown in Figs. 12 and 13, respectively. For the acetonitrile-processed Li₂Pc-doped PT film, the S 2p core-level peak was derived only from S sites of thiophene rings of the polymer backbone. The spectrum was basically composed of 2p_{1/2} and 2p_{3/2}, which were clearly separated as shown in Fig. 12(a). The low energy components of 2p_{1/2} and 2p_{3/2} existed clearly shifted by 1 eV lower than the nondoped original polymer peaks. This means that the negative charge increased at partial S sites of polymer backbone. In contrast, in the toluene-processed Li₂Pc-doped PT film, only signals consistent with nondoped PT were observed with no lower energy components [Fig. 13(a)]. According to the results, it suggested that negative charge transfer occurred from some of the dopants to the polymer backbone. Lower binding energy components were also observed for the CuPc-doped PT film, as indicated in Fig. 12(e). Higher energy components were observed for the FePc-doped PT film processed in acetonitrile compared to that processed in toluene, as shown in Figs. 12(d) and 13(d). This indicates that negative charge transfer occurred from the polymer to

FIG. 13. (Color online) S 2p core-level spectra of toluene-processed PT-PcM films: (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, (e) CuPc-doped PT, and (f) as-grown PT.

the dopant in the film prepared using acetonitrile. For the MgPc- and CoPc-doped PT films, shifts to higher energy were observed using acetonitrile instead of toluene, depicted in Figs. 12(b), 12(c), 13(b), and 13(c).

FIG. 12. (Color online) S 2p core-level spectra of acetonitrile-processed PT-PcM films: (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, (e) CuPc-doped PT, and (f) as-grown PT.

FIG. 14. (Color online) Central metal core-level spectra of acetonitrile-processed PT-PcM films: (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, and (e) CuPc-doped PT.

FIG. 15. (Color online) Central metal core-level spectra of toluene-processed PT-PcM films. (a) Li₂Pc-, (b) MgPc-, (c) CoPc-, (d) FePc-, and (e) CuPc-doped PT.

Finally, the electronic states at the central metal sites of PcM were investigated. XPS core-level spectra of the central metal ions in acetonitrile- and toluene-processed PcM-doped PT films are shown in Figs. 14 and 15, respectively. These spectral profiles varied with metal species. In the Li 1s core-level spectrum of the acetonitrile-processed Li₂Pc-doped PT film, the binding energy of the main component shifted to lower energy compared to that for the toluene-processed compound [Figs. 14(a) and 15(a)], which suggests the negative charge is transferred to the central metal atoms. In the Mg 2p core-level spectrum of the acetonitrile-processed MgPc-doped PT film [Figs. 14(b) and 15(b)], a lower binding energy component appeared compared to that processed in toluene, implying negative charge was transferred to the central metal Mg. In the case of central metal ions with d-electrons such as CoPc-, FePc-, and CuPc-doped PT films, charge transfer at the central metal ion was confirmed. Lower energy components were clearly observed in the 2p_{3/2} and 2p_{1/2} peaks of Co, Fe, and Cu in the acetonitrile-processed films compared to those processed in toluene, as shown in Figs. 14(c)–14(e) and 15(c)–15(e).

IV. CONCLUSIONS

The PL properties of conducting polymer PT films incorporated with PcMs such as CuPc, MgPc, FePc, Li₂Pc, and CoPc were studied by PL and TCSPC measurements. The polymer films were prepared by electrochemical polymerization and PcMs were doped into the polymer films by a diffusion method using acetonitrile or toluene as a solvent. The position of PL emission peaks depended strongly on the sol-

vents used in the doping process. Using acetonitrile, PL emission originated from the Q band, whereas PL emission was assigned to the Soret band when toluene was used as a solvent. The corresponding absorption spectra of Li₂Pc- and MgPc-doped PT films confirmed that the emission states had the same origin because the absorption peaks were observed at 445 and 465 nm in the acetonitrile-processed films and around 300 nm in the toluene-processed ones. Li₂Pc- and MgPc-doped PT films belong to the same category not only because their absorption peaks that correspond to PL emission are the same, but also because their average lifetimes measured by TCSPC are similar. In these films, the TCSPC measurements revealed that singlet-singlet emission occurred through an intraligand transition process. An obvious change in emission pattern change between Q and Soret bands that depends on the solvent used in the doping process was observed for all five PcM-doped PT films. Among them, the film that showed the largest change in emission pattern was the Li₂Pc-doped PT film, where intense emission peaks attributed to either Q or Soret bands were observed from films processed in acetonitrile or toluene, respectively. In the case of the acetonitrile-processed MgPc-doped film, the PL intensity was weak compared to that of the Li₂Pc-doped PT film. For CoPc- and FePc-doped PT films with central metal ions containing d-electrons, PL and absorption spectra exhibited different emission peak profiles compared to those of Li₂Pc- and MgPc-doped PT films. In these cases, the absorption peaks corresponding to PL emissions showed different profiles. The CuPc-doped PT films showed minor differences in PL emission. Using acetonitrile, TCSPC measurements showed that singlet-singlet emission occurred through an intraligand transition process because average lifetimes were comparable at around 140 ns and independent of the central metal ions in the case of Li₂Pc-, MgPc-, and CoPc-doped PT films, except for the FePc- and CuPc-doped PT ones. The PL emissions of FePc- and CuPc-doped PT films were possibly singlet-singlet transitions mixed with singlet-triplet transitions because the average lifetimes were longer and shorter, respectively. Conversely, using toluene, it was found that ligand-ligand emission took place in the cases of Li₂Pc-, MgPc-, and FePc-doped PT films. XPS measurements were conducted to understand the reason for the large changes in PL emission. The results of the XPS measurements accounts for the drastic change in the emission pattern considering the basic theory of the PL emissions of phthalocyanine and porphyrin. A lower binding energy component appeared in the C 1s core-level spectra of acetonitrile-processed PcM-doped PT films. This component shifted to higher energy and overlapped the main peak in the toluene-processed PcM-doped PT films. The lower binding energy component corresponded to photoelectrons related to the C atoms in ligand benzene rings. In contrast, lower binding energy components also appeared in the N 1s core-level spectra of acetonitrile-processed PcM-doped PT films, and this component shifted to higher energy in the spectra of toluene-processed PcM-doped PT films. These lower energy components were assigned to the core-level peaks related to the N atoms at meso positions bridging between pyrrole

rings. This suggests that the electron charge at the N-sites of meso positions in toluene-processed complexes was less than that in acetonitrile-processed polymers. The energy shifts at the benzene C sites and the meso N sites suggest that the electronic states of phthalocyanine in the toluene-processed complexes behave similarly to porphyrins, so that the Soret band becomes dominant in the PL emission process.

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