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Processible poly[(*p*-phenyleneethynylene)-*alt*-(2,5-thienyleneethynylene)]s of high luminescence: their synthesis and physical properties

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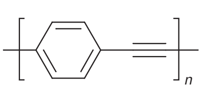
Several alternating copolymers, poly[(*p*-phenyleneethynylene)-*alt*-(2,5-thienyleneethynylene)]s (PPETEs), have been synthesized by using a Heck-type coupling reaction under mild conditions. The polymers are characterized by using ^{1}H and ^{13}C NMR, UV–VIS absorption and fluorescence spectroscopy. PPETEs produced under the mild conditions exhibit longer conjugation length (*ca.* 10 nm in UV–VIS absorption λ_{max}) than the same polymers synthesized at high temperature. The chain rigidity of the copolymers is moderate with Mark–Houwink constant $\alpha = 0.82$–0.94, which is moderately higher than PTE **2** ($\alpha = 0.68$) but significantly lower than PPE **3** ($\alpha = 1.92$). The PL quantum efficiencies of PPETE copolymers are found to be $\phi_{fl} = 0.37$–0.48, which is comparable to PPE homopolymers and much higher than for PTE ($\phi_{fl} = 0.18$). Synthesis of copolymer PPETE thus successfully combines both the high luminescence of PPE and good solubility of PTE into a single polymer chain.

Introduction

Recent research indicates a considerable interest in the photoluminescent and electroluminescent properties of conjugated polymers, following the first demonstration of the light-emitting properties from poly(*p*-phenylenevinylene) (PPV).[1] Among the reported luminescent polymers, which have been used as active layers in light-emitting diodes,[2] are poly(*p*-phenylenevinylene) (PPV),[3] poly(*p*-phenylene) (PPP),[4] poly(thiophene) (PT)[5] and poly(*p*-phenyleneethynylene) (PPE).[6] Current research interests in luminescent materials include tailoring of the spectral characteristics and improving their processibility and long-term stability. One of the most challenging problems in the field is to optimize the radiative decay of the materials in order to achieve high quantum efficiencies in both photoluminescence and electroluminescence. This obviously requires an understanding of the various structural effects on the luminescence efficiency of the materials.

Poly(aryleneethynylene) is a special class of π-conjugated polymers in which aromatic rings alternate with carbon–carbon triple bonds. The linear rod-like bonding geometry of the triple bond has the advantage of extending the molecular rigidity in both short and long ranges. For example poly(*p*-phenyleneethynylene)s (PPEs) **1** have a linear rod molecular structure which has a characteristically large Mark–Houwink constant ($\alpha = 1.92$)[7] in comparison with $\alpha = 0.96$ for polythiophene.[8] The increased molecular rigidity in PPEs could be responsible for their high solution PL quantum efficiencies.[9] Since the α constant is one of the important parameters in describing undisturbed polymer conformations in solution, correlation between the α values and solution quantum yields of π-conjugated polymers could be a very useful probe to study the effect of the molecular rigidity of a polymer in solution on its PL efficiency.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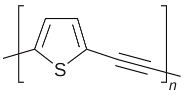
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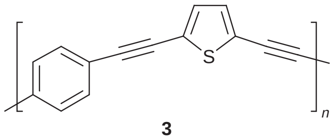
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Another example of a poly(aryleneethynylene) is poly(thienyleneethynylene) (PTE) **2** which exhibits green photoluminescence[10,11] with moderate solution quantum efficiency ($\phi_{fl} \approx 0.2$).[12] The α value of PTE **2** measured in THF solvent, however, is about 0.68, which is typical for a random-coil molecular conformation. Clearly the presence of the α-linked thiophene bridges has a large impact on the long-range molecular rigidity and the corresponding physical properties.

It is obviously desirable to develop poly(aryleneethynylene) materials which exhibit both the high luminescence of PPE **1** and processibility of PTE **2**. A standard approach is to place both *p*-phenylene–ethynylene and α-linked thiophene–ethynylene units into a single polymer chain as shown in **3**. The short-range chain rigidity is increased by extending the linear rod-like chain segment from thiophene–ethynylene–thiophene in **2** to thiophene–ethynylene–phenylene–ethynylene–thiophene in **3**, and the PL efficiency of **3** is expected to be significantly higher than **2**. Inclusion of α-linked thiophenes in **3** will modify the rigid-rod backbone of PPE so as to improve the solubility and processibility relative to PPE **1**. Although a few examples of copolymer **3** have been synthesized by this group[13] and others,[7,11,14] no systematic study has been carried out to evaluate their PL efficiencies and their dependence on chain rigidity. Here we report our results on the synthesis of three variously substituted examples of **3** under mild conditions, and characterization of their photoluminescent properties and molecular chain rigidities.

Results and Discussion

Polymer synthesis and characterization

Poly[(*p*-phenyleneethynylene)-*alt*-(thienyleneethynylene)]s (PPETEs **4**–**6**) were prepared by Heck-type coupling.[15] Typically a substituted 2,5-diiodothiophene reacted with a diethynylbenzene in toluene in the presence of a catalytic system $PdCl_2(PPh_3)_2$–CuI–Et_3N to lead to a polymer back-

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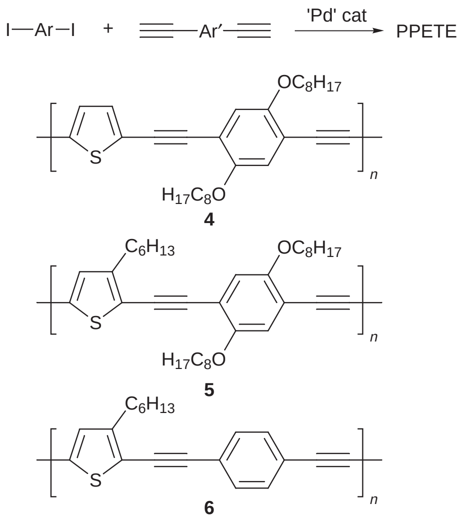

Scheme 1 Synthesis of co-polymer PPETEs

bone where α-thiophene and benzene rings alternately occur along the polymer chain. Using diiodothiophene (as opposed to dibromothiophene) allows the polymerization to be carried out at room temperature, thus minimizing the unwanted side reactions.

PPETEs were yellow–orange in color in the solid state. The polymers showed good solubility in common organic solvents such as toluene, THF and chloroform. Uniform films could be cast from their solutions. IR and ^{1}H NMR spectra of the polymers indicated that the polymerization was completed under the mild conditions used as evidenced from the disappearance of the acetylenic groups. Sharp resonance signals in the ^{1}H and ^{13}C NMR spectra (Fig. 1) imply high linear regularity along the polymer chains. Originating from the unsymmetrical characteristics of the 3-hexyl-2,5-thienylene unit, PPETE **5** and **6** are expected to have a random distribution of head-to-head and head-to-tail sequences along the polymer chain. Both ^{1}H and ^{13}C NMR spectra failed to detect the structural regioregularity since the alkyl substituents on the thiophenes are well seperated from each other. Details of the effect of the structural regioregularity on physical properties, including photoluminescence and molecular rigidity, will be discussed in a forthcoming paper to deal with the synthesis and characterization of regioregular **6**.

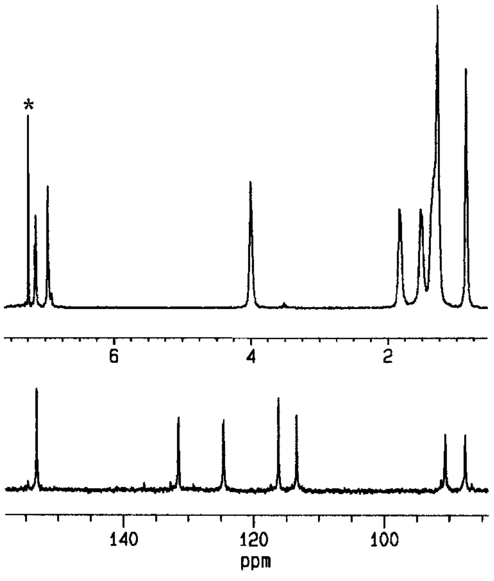

Fig. 1 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of PPETE **4** in $CDCl_3$. The starred signal at 7.25 ppm (top spectrum) is attributed to $CHCl_3$. The alkyl region in the ^{13}C NMR spectrum is not shown for clarity.

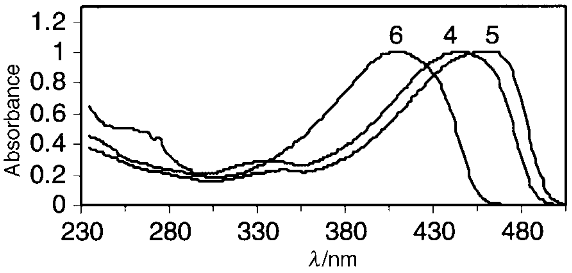

Fig. 2 UV–VIS absorption spectra of **4–6** measured in THF

Fig. 2 shows the UV–VIS absorption spectra of PPETEs. The absorption λ_{max} values of the polymers are listed in Table 1. It is noted that the absorption λ_{max} values of PPETE **4** and **6** are at 444 and 413 nm, which are about 11 nm longer than the same polymers[7,11] prepared at elevated temperature. Clearly the mild polymerization conditions are important in synthesizing poly(aryleneethynylene)s since phenylacetylenes[16] are susceptible to thermal reactions. This is also in agreement with the sharper alkyl ^{1}H NMR signals observed from **4** than that from the PPETE[14e] synthesized at 60 °C.

Molecular weight and chain stiffness

The molecular weights of the polymers were measured in THF eluent by using size exclusion chromatography with on-line refractive index, viscosity and light-scattering detectors (referred to as SEC^3). By using the SEC^3 setting, the true molecular weights were obtained *versus* the elution volume. A typical SEC^3 chromatogram is shown in Fig. 3, indicating a monomodel distribution in molecular weight. The comparable peak molecular weights from refractive index (RI), viscosity (DP) and light-scattering (LS) detectors suggest a linear structure without branching. The polydispersity indices of the polymers (listed in Table 1) are about 2, which is typical[17] for condensation polymerization and in agreement with the proposed linear polymer structure.

For π-conjugated polymers, a fundamental issue is how much molecular rigidity is imparted by the extended π-conjugation. Until today little attention has been paid to the solution properties[8,18] of these π-conjugated polymers. Information about the unperturbed molecular conformations or dimensions in dilute solutions could be a very useful probe to gain an insight into the extended chain stiffness of poly(aryleneethynylene)s. A typical Mark–Houwink plot for PPETE is shown in Fig. 3, which exhibits a good linear relationship between intrinsic viscosity and molecular weight. The α values in the Mark–Houwink equation $[\eta]=K\ M^{\alpha}$ were determined to be about 0.82–0.94 for PPETEs which is only moderately higher than poly(3-hexylthienyleneethynylene) (P3HTE)[12] ($\alpha=0.68$) but significantly lower than PPE[7] ($\alpha=1.92$). The low α value implies that the polymer chains of PPETEs are far less stiff than the rigid-rod polymer PPE as a result of the main chain modification. In other words, replacing alternate phenyl groups in PPE by thiophene rings has a large impact in reducing the long-range chain stiffness of PPE. This is in agreement with the observed good solubility for PPETE **6** in which there is no substituent on the phenyl ring.

Photoluminescence

PPETEs exhibited strong green luminescence in solution in organic solvents. The fluorescence spectra were obtained from diluted and deoxygenated THF solutions (Fig. 4). All spectral data are summarized in Table 1. Similar to the fluorescence of PPE[9] and PTE,[12] two well-resolved bands (high and low energy emissions) were observed in PPETEs, suggesting the

Table 1 UV–VIS, fluorescence and molecular weight data for PPETEs

polymer	absorption[a] λ_{max}/nm	fluorescence[a] λ_{max}/nm	excitation λ_{max}/nm[b]	ϕ_{fl}[c]	MW (PDI)	Mark–Houwink constant α
PPETE 4	444 (THF)	482, 514 (THF)	450 (THF)	0.37 (THF)	43 900 (2.12)	0.88
	444($CHCl_3$)	485, 518 ($CHCl_3$)	450 ($CHCl_3$)	0.37 ($CHCl_3$)		
PPETE 5	460 (THF)	489, 520 (THF)	468 (THF)	0.48 (THF)	61 600 (2.15)	0.82
	457 ($CHCl_3$)	492, 524 ($CHCl_3$)	468 ($CHCl_3$)	0.47 ($CHCl_3$)		
PPETE 6	414 (THF)	451, 478 (THF)	398 (THF)	0.46 (THF)	78 500 (2.27)	0.94
	413 ($CHCl_3$)	455, 480 ($CHCl_3$)	398 ($CHCl_3$)	0.47 ($CHCl_3$)		
P3HTE[d]	438 (THF)	525, 535 (THF)	420 (THF)	0.18 (THF)	20 100 (1.9)	0.68

[a]Solvent is shown in parentheses. [b]Fluorescence excitation λ_{max} observed while monitoring at fluorescence λ_{max}. [c]Quantum yields are measuured in $CHCl_3$ and THF solvent while excited at excitation λ_{max}. [d]Poly(3-hexylthienyleneethynylene).[12]

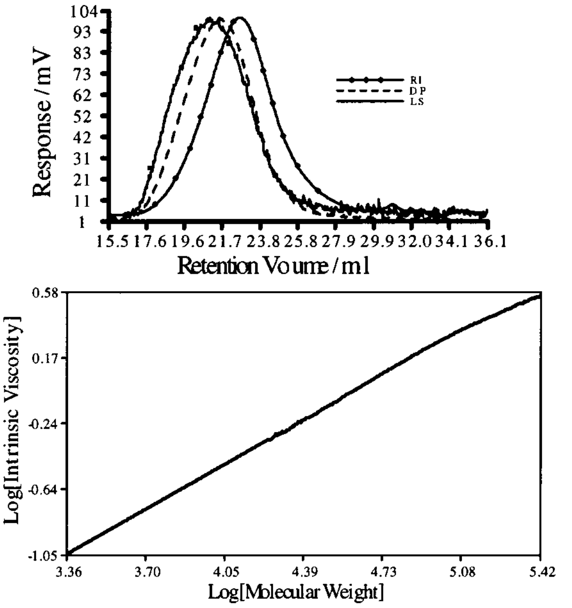

Fig. 3 SEC[3] chromatogram (top) and Mark–Houwink plot (bottom of PPETE **5**. The intrinsic viscosity in the plot is expressed in dl l^{-1}.

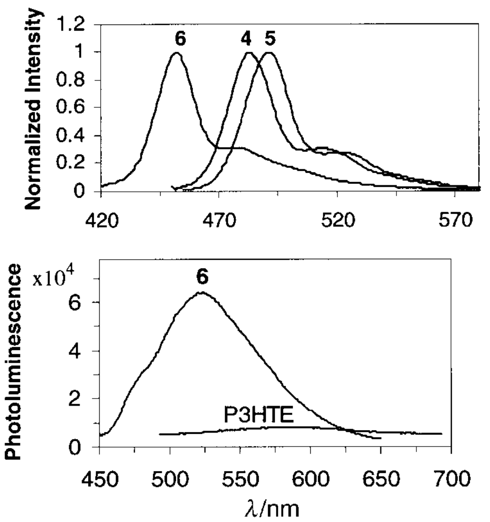

Fig. 4 Fluorescence spectra of PPETEs in THF solvent (top, normalized) and film state (bottom)

existence of similar pathways for the radiative decay of the excited states. The PL quantum yields were determined relative to quinine sulfate. The PPETEs were found to be highly luminescent in solutions with quantum efficiencies ranging from 0.37 to 0.48, which are quite comparable to those of PPE homopolymers[19] (ϕ_{fl}=0.35–0.40). The quantum yields (ϕ_{fl}) of PPETEs were measured in both THF and $CHCl_3$, giving very similar values (Table 1). It should be noted that the ϕ_{fl} values of PPETE are significantly larger than those of an isomeric structural analogue, poly[(*m*-phenyleneethynylene)-*alt*-(thienyleneethynylene)],[14d] whose ϕ_{fl} value in $CHCl_3$ is reported to be only 0.18. The greater enhancement observed from the *p*-phenylene-containing PPETE is presumably due to the longer conjugation length permitted by *p*-phenylene than by *m*-phenylene in the PPETE polymers.

It is also interesting to make a comparison between the photophysical properties of PPETE (**3**) and P3HTE (**2**).[12] Only slight changes in the absorption λ_{max} are observed between P3HTE and PPETEs (Table 1), indicating similar conjugation lengths between the two polymer systems. The PL quantum efficiencies of PPETEs, however, are about 2.5 times as high as P3HTE (ϕ_{fl}=0.18). Clearly alternate replacement of the thiophene rings along the P3HTE chain with phenyl rings has a large impact on the nonradiative decay process. The enhancement is even more pronounced in the solid state, as the PPETE film emits about 15 times more strongly than P3HTE film with a head-to-tail chain sequence[12] (Fig. 4) under the identical conditions.

Conclusion

Alternating copolymer PPETEs synthesized under mild reaction conditions exhibit longer conjugation length (*ca.* 10 nm in UV–VIS absorption λ_{max}) than the same polymers synthesized at high temperature. The copolymers have moderate chain rigidity with Mark–Houwink constant α=0.82–0.94, which is higher than PTE **2** (α=0.68) but drastically lower than PPE **3** (α=1.92) homopolymers. The PL quantum efficiencies of PPETE copolymers are found to be much higher than PTE **2**, attributed partially to the increased local (or short-range) chain rigidity in the copolymers. More interestingly, the quantum efficiencies of PPETEs are found to be comparable with, or even slightly higher than, homopolymer PPE **3**. Thus synthesis of copolymer PPETE successfully combines both good solubility of PTE and high luminescence of PPE into a single polymer chain, making the material attractive for device applications. The PL enhancement in the solid state is even more pronounced as the PPETE film emits about 15 times as strongly as P3HTE film.

Experimental

Materials and instrumentation

2,5-Diiodo-3-hexylthiophene,[20] 1,4-diethynyl-2,5-bis(octyloxy)-benzene[9] and 1,4-diethynylbenzene[21] were synthesized according to literature procedures. 2,5-Diiodothiophene and solvents were purchased from Aldrich Chemical Company. Solvents were dried, distilled and stored under argon. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. UV–VIS spectra were recorded in THF or $CHCl_3$ solvents on a Beckman DU640 spectrophotometer at 23 °C. NMR spectra were acquired on a Bruker ARX400 spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C. Fluorescence spectra were recorded on a PTI steady state fluorometer at 23 ± 1 °C. UV–VIS and fluorescence spectra of polymer films were recorded on glass substrates in air. Size exclusion chromatography (SEC) was carried out on a Viscotek SEC assembly consisting of a Model P1000 pump, a Model T60 dual detectors and a Model LR40 laser refractometer. Polymer concentrations for SEC experiments were prepared in a concentration of 2–3 mg ml^{-1}.

Preparation of poly[(3-hexyl-2,5-thienyleneethynylene)-*alt*-(1,4-phenylene ethynylene)] 6, a general procedure for PPETEs

3-Hexyl-2,5-diiodothiophene (2.776 g, 2.2 mmol), 1,4-diethynylbenzene (0.277 g, 2.2 mmol) and triethylamine (2.6 g, 26 mmol) were dissolved in 40 ml of dry toluene in a 100 ml oven-dried, one-necked, round-bottomed flask which was equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by twice repeating a cycle of freezing and thawing under vacuum, followed by filling with an argon atmosphere. Catalysts $PdCl_2(PPh_3)_2$ (14.0 mg, 0.02 mmol) and CuI (3.8 mg, 0.02 mmol) were added at room temperature in a glove bag under a dry argon atmosphere. After stirring the solution at room temp. for 4 h (lots of salts formed during this period), the reaction mixture was heated to 42 °C overnight. The resulting orange–brown solution was twice precipitated from methanol to give a yellow resin (92% yield). ^1H NMR ($CDCl_3$) δ 0.89 (br, 3H, CH_3), 1.25–1.40 [br, 6H, $(CH_2)_3$], 1.67 (br, 2H, CH_2), 2.73 (br, 2H, CH_2), 7.07 (s, 1H, thiophene H), 7.48 (s, 4H, phenyl H). Quantitative ^{13}C NMR ($CDCl_3$) δ 13.6 (1C), 22.1 (1C), 28.4 (1C), 29.1 (1C), 29.6 (1C), 31.1 (1C), 83.8 (1C), 84.4 (1C), 93.3 (1C), 95.7 (1C), 119.6 (1C), 122.3 (1C), 122.5 (1C), 122.7 (1C), 130.9 (4C), 132.7 (1C), 147.6 (1C). Anal. calc. for $(C_{20}H_{18}S)_n$: C, 82.71; H, 6.25. Found: C, 82.05; H, 6.19%.

Poly[(2,5-thienyleneethynylene)-*alt*-(2,5-dioctyloxy-1,4-phenyleneethynylene)] 4. PPETE 4 (yellow–orange resin) was synthesized in 89% yield using the same conditions as described for **6**. ^1H NMR ($CDCl_3$) δ 0.87 (br, 6H, CH_3), 1.28 [br, 16H, $(CH_2)_4$], 1.52 (br, 4H, CH_2), 1.83 (br, 4H, CH_2), 4.01 (br, 4H, -CH_2O-), 6.97 (s, 2H), 7.14 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 153.2 (2C), 131.5 (2C), 124.6 (2C), 116.1 (2C), 113.4 (2C), 90.6 (2C), 87.5 (2C), 69.5 (2C), 31.7 (2C), 29.1 (6C), 25.9 (2C), 22.5 (2C), 13.9 (2C). Anal. calc. for $(C_{30}H_{38}O_2S)_n$: C, 77.88; H, 8.28. Found: C, 77.01; H, 8.15%.

Poly[(3-hexyl-2,5-thienyleneethynylene)-*alt*-(2,5-dioctyloxy-1,4-phenyleneethynylene)] 5. PPETE 5 (yellow–orange resin) was synthesized in 95% yield using the same conditions as described for **6**. ^1H NMR ($CDCl_3$) δ 7.05 (s, 1H), 6.95 (s, 2H), 4.00 (br, 4H, -CH_2O-), 2.75 (br, 2H, -CH_2-thiophene), 1.82 (br, 4H), 1.65 (br, 2H), 1.51 (br, 4H), 1.10–1.42 (br, 22H), 0.87 (br, 12H, CH_3). Anal. calc. for $(C_{36}H_{50}O_2S)_n$: C, 79.07; H, 9.21, Found: C, 78.51, 9.08%.

Photoluminescence quantum yield measurements

All slits were kept at 2 nm for excitation and emission. Photoluminescence spectra were corrected for the spectral dispersion of the Xe lamp. All sample solutions were freshly prepared in dry THF, purged with high purity argon and used within four hours. Absorbances of all sample solutions were kept between 0.05–0.08. Quantum yields of fluorescence were determined relative to quinine sulfate[22,23] in 0.5 M H_2SO_4 at 23 ± 1 °C, assuming a quantum yield of 0.546 when excited at 365 nm. Refractive indices[24] of pure 0.5 M H_2SO_4 and THF were used for the standard and sample solutions during the calculation of quantum yield. The quantum yields reported here are averaged over at least three measurements, with a standard deviation below 0.02. The quantum efficiency of a sample was calculated by using the following equation:

$$\phi_s = \phi_r\ (A_r/A_s)\ (F_s/F_r)\ (n_s^2/n_r^2)$$

Here A_r and A_s are the absorbances of the sample and reference solutions at the excitation wavelength; F_s and F_r are the corresponding emission integration areas; and ϕ_s and ϕ_r are quantum efficiencies of the sample and reference compound; n_s and n_r are refractive indices of the sample and standard solutions.

Solid state fluorescence spectra were acquired from spin-cast films whose photoabsorbance was between 0.7–1.0 at absorption λ_{max}. Emission was detected at 90° from the incident beam by the front face fluorescence method with the film placed at an angle of about 45° to both the incident beam and the detector. The relative emission intensity was estimated by using

$$\phi_s/\phi_r = (A_r/A_s)\ (F_s/F_r)\ (n_s^2\ /n_r^2) \approx (A_r/A_s)\ (F_s/F_r)$$

similarly defined in the solution measurement. Here the refractive indices are assumed to be similar for both PPETEs and P3HTE.

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