Emissive Tetraphenylethylene (TPE) Derivatives in a Dissolved State Tightly Fastened by a Short Oligo(Ethylene Glycol) Chain

Journal:	*Organic Chemistry Frontiers*
Manuscript ID	QO-RES-07-2020-000839.R2
Article Type:	Research Article
Date Submitted by the Author:	29-Jul-2020
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ARTICLE

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The structural change in the excited state evidently plays a crucial role for quenching process of organic molecules exhibiting aggregation-induced emission (AIE, thus AIEgens) in the solution state. In this report, we synthesized a series of tetraphenylethylene (TPE) macrocycles having covalent oligoethylene glycol (OEG) linkage between vicinal phenyl rings with various chain length and substituting positions. As a result, the obtained TPE macrocycles which is tightly fastened by short OEG chain showed strong emission even in the solution state. The tight fastener efficiently restricted π twist around the central C=C bond in TPE macrocycles, which was also supported by theoretical computations. These results provide very important information about the origin of AIE property of TPE derivatives, which will lead to rational design for new AIEgens.

Introduction

In the past 20 years, a multitude of materials based on aggregation-induced emission (AIE) has emerged, showing extraordinary emission in the aggregated or solid state but only weak or no emission in the solution state.[1–5] Nonetheless, the phenomenon is a “revisit” of preceding researches; in fact, the intra- and intermolecular aspects of the underlying phenomena for organic dyes have been intensively discussed over one hundred years.[6] For oligo(phenylene vinylene)s, the intra- and intermolecular factors for emission from film and aggregate were already reported in 1990’s.[6–9] After coining “AIE” by Tang and coworkers in 2001 by using a pentaphenylsilole derivative,[10] as well as aggregation-induced emission enhancement (AIEE) reported by Park and coworkers in 2002,[11] this attractive switching property of AIEgens has prompted researchers to explore a new class of optical materials utilizing AIEgens, including optoelectronics,[12–14] fluorescent probes,[15–17] and biosensors.[18–20] In the beginning of AIE studies, rotation of phenyl rings *in the ground state* has been believed to be essential for the quenching of AIE luminogens (AIEgens) in the solution state, which should be restricted in the aggregated or solid state (restriction of intramolecular rotation, RIR).[21] However, thanks to the development of computer performance for theoretical computation, researchers now can readily know the molecular structure and dynamics in the excited state, and a large structural change of AIEgens in the excited state has been recently recognized as the essential factor for the quenching of AIEgens in the solution state.[22–25] For examples, Blancafort and co-workers revealed that restricted access to conical intersection (RACI) results in the strong emission of siloles and furans having accumulated phenyl rings, by using state-of-art theoretical computations,[25] thus highly twisted π plane (π twist) is responsible for the quenching of these AIEgens in the solution state.

Tetraphenylethylene (TPE) is one of the most known AIEgens due to the ease of synthesis and derivatization, it has been employed as a typical AIEgen to construct emissive systems in a plenty of researches. On a historical viewpoint, the emission enhancement was already known in 50 years ago.[26–28] The π twist of the central C=C bond of TPE in the excited state was already known in 1990’s or before by using ultrafast spectroscopies and related techniques,[29–31] as well as viscosity-dependent fluorescence enhancement.[32,33] Fox and coworkers reported the emission enhancement of TPE macrocycles in which geminal phenyl rings are linked at *meta*-position, and phenyl ring torsion was suppressed by short chain length, leading to strong emission in solution.[34,35] As mentioned above, the intra- and intermolecular factors for emission from film and aggregate of oligo(phenylene vinylene)s were already studied in 1990’s.[6–9] On the other hand, AIE property of TPE was reported in 2006 by Tang et al.,[36] which followed the report of pentaphenylsilole,[10] thus the mechanism of AIE property of TPE was explained by applying RIR process. Unfortunately, the accumulation of preceding researches[7–9,26-35] was not referred.[36]

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† Electronic Supplementary Information (ESI) available: [Experimental details, NMR spectra, crystallographic data, chiral column chromatograms, NMR spectra upon photoirradiation, and calculated geometrical parameters for TPE macrocycles]. See DOI: 10.1039/x0xx00000x

Without proper substitution on the vicinal phenyl rings of TPE, (*E*)-(*Z*) isomerization (EZI) cannot be observed by usual spectroscopies for tetrasubstituted TPE or bare TPE, and even with disubstituted TPE, (*E*) to (*E*) or (*Z*) to (*Z*) transition cannot be detected and is ignored, despite π twist in the excited state. Recently, we disclosed that π twist of TPE in the excited state is essential for quenching in the solution state, thus the restriction of π twist by such as aggregation or crystallization is essential for the occurrence of AIE property, confirmed by the spectroscopy for disubstituted TPE derivatives and theoretical computations,[23] followed by Tang and coworkers,[37] and another research group.[38]

The restriction of π twist of AIEgens can be also carried out in solution[39–42] or dispersed state,[43–48] not only in aggregated or solid state. In solution state, supramolecular interaction is the most powerful method to suppress π twist. For such examples, Shinkai and coworkers reported “cyclization-induced emission” of a TPE derivative having zinc dipicolylamine group which can interact with dicarboxylic acids.[39] Zheng and coworkers reported the emission of TPE derivatives with oligoethylene glycol (OEG) chain after complexing with γ-cyclodextrin (γ-CD).[40] Wu and coworkers presented emission of TPE derivatives having bisurea moiety recognizing oxoacid anions such as $PO4^{3-}$ and $SO4^{2-}$.[41] Hahn and coworkers reported the emission of a TPE derivative tethering *N*-heterocyclic carbene (NHC) interacting with metal cations.[42] Besides the supramolecular interaction, covalent linkage to restrict π twist of TPE derivatives has been very recently reported by Zheng, in which *cis*-TPE dicycle showed strong emission in a solution, whereas *gem*-TPE dicycle did not. This fact provides a strong evidence of the important role of π twist around central C=C bond in TPE derivatives for quenching in the solution state.[49] Zheng and coworkers also applied TPE macrocycles as the sensor for chiral acid[50] and DNA[51] in a solution. In addition to supramolecular interaction, bulky substituents also suppress π twist, as can be seen in strong emission of *ortho*- substituted TPE,[52] which was well reproduced by state-of-art theoretical computations.[53,54] However, the quantitative estimation of the restriction of π twist by such covalent linkage in the excited state have not yet explored probably due to the cumbersome synthetic procedure to change the tightness of covalent linkage “fastener” bit by bit, which is very difficult to achieve by using a fragile cyclic structure formed by relatively weak supramolecular interaction. Other reports for TPE macrocycles focused AIE property and chiroptical property in solid or aggregated state.[55,56]

Herein, we prepared a series of TPE macrocycles in which the vicinal phenyl rings are linked by OEG chains at *para*-, *meta*-, and *ortho*- positions. The effect of OEG chain length and the substituting position were investigated in detail, along with theoretical computations for the molecular structure in the excited state. Our results presented here will provide a new perspective for molecular motion originating AIE property and a rational molecular design for a novel TPE macrocycles.[57]

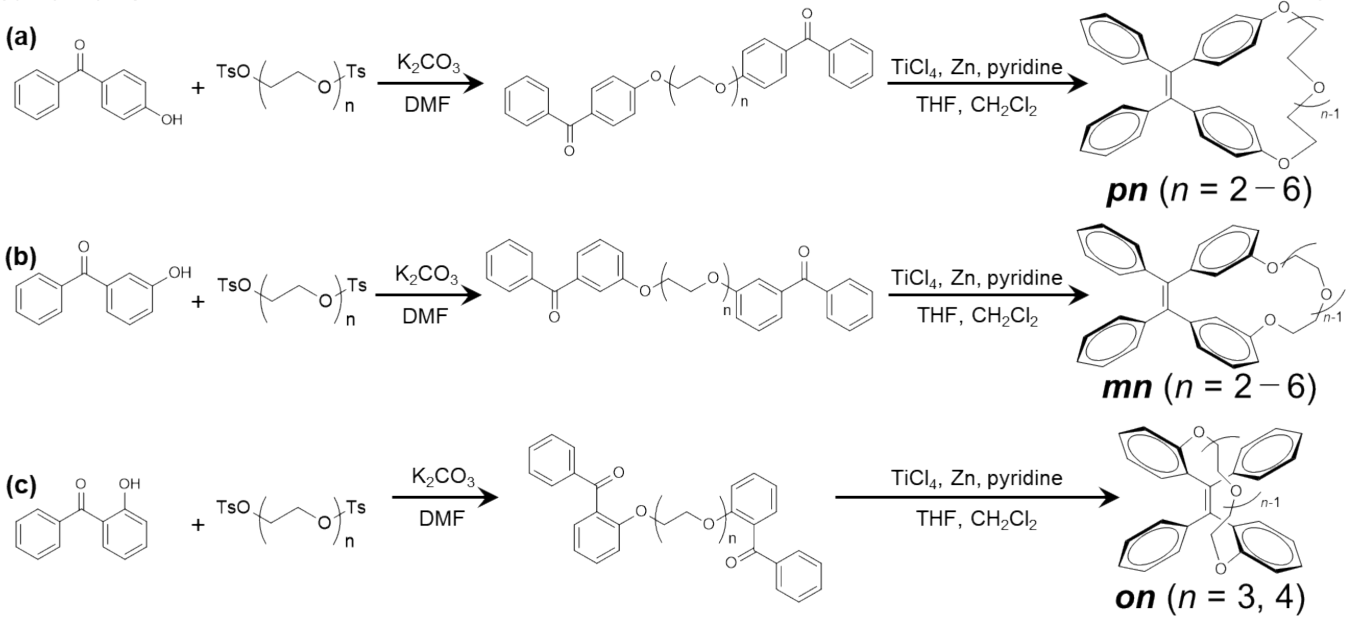


Fig. 1 Synthetic routes for (a) ***pn*** (***n*** = 2–6), (b) ***mn*** (*n* = 2–6), and (c) ***on*** (*n* = 3,4).

Results and Discussion

TPE macrocycles (***pn*** (*n* = 2–6), ***mn*** (*n* = 2–6), ***on*** (*n* = 3,4)) were synthesized from Williamson ether synthesis of the corresponding monohydroxy benzophenones and oligo(ethylene glycol) (OEG) bis(toluenesulfonate)s, followed by intramolecular McMurry coupling mediated by titanium (IV) chloride and zinc (Fig. 1). To improve the yield of intramolecular cyclization, the precursor solution was slowly added to the reaction mixture for 6 h. The obtained compounds were characterized by ^{1}H and ^{13}C NMR spectroscopies (Fig. S1–S24) and high resolution mass spectroscopy (HRMS). From the HRMS results, no polymeric compounds were found for all TPE macrocycles, indicating successful progress of the intramolecular cyclization. NMR studies revealed that all TPE macrocycles consisted of one isomer, except for ***o*4**. The NMR spectrum of ***o*4** implied the existence of two isomers with the ratio of 89/11, and the major isomer was isolated by a silica gel column chromatography. The synthesis of ***o*5** and ***o*6** was also attempted, but the intramolecular cyclization for ***o*6** was not successful, while the isomer of ***o*5** was not isolated at all after the intramolecular cyclization.

To determine the chemical structure of the TPE macrocycles, we firstly carried out the theoretical computations regarding the energy difference of *cis* and *trans* isomers in the ground state by density functional theory (DFT) method at the B3LYP[58,59]/6-31G(d) level using Gaussian 16.[60] As the result of calculation, for ***p*2**–***p*6** and ***m*2**–***m*6**, *cis* isomers were found to be more stable than the *trans* isomers (Table 1). For ***p*2** and ***p*3**, the calculation of *trans* isomer was not converged due to its too high energy. On another front, the *trans* isomer of ***o*3** was found to be more stable than its *cis* isomer, and almost no energy difference was found for ***o*4**, which corresponds to the formation of isomeric mixtures indicated by NMR studies.

Table 1. Summary of energy difference between *cis* and *trans* isomers.

Molecule	isomer[a]	E_{trans}-E_{cis} (eV)
***p*2**	*cis*	-[b]
***p*3**	*cis*	-[b]
***p*4**	*cis*	0.70
***p*5**	*cis*	0.42
***p*6**	*cis*	0.31
***m*2**	*cis*	0.49
***m*3**	*cis*	0.49
***m*4**	*cis*	0.30
***m*5**	*cis*	0.21
***m*6**	*cis*	0.16
***o*3**	*trans*	-0.40
***o*4**	*cis* (major)	-0.007

[a] The result of synthesis. [b] The energy of *trans* isomer was not obtained due to too high instability.

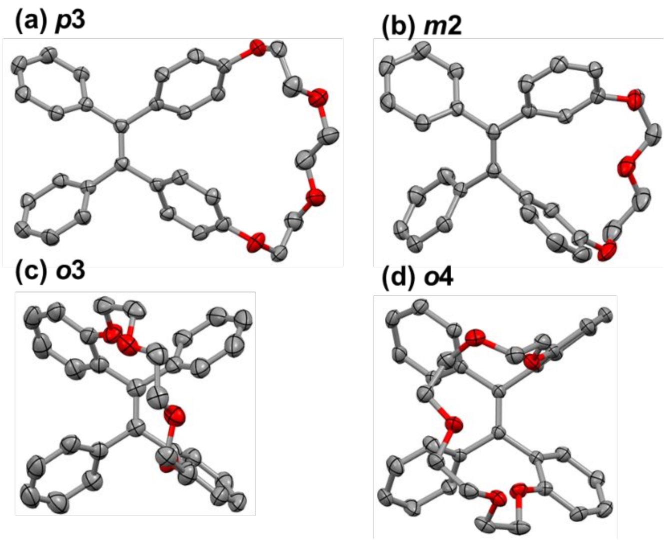


Fig. 2 Crystal structure of (a) ***p3***, (b) ***m2***, (c) ***o3*** and (d) ***o4***. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

The compounds of ***p3***, ***m2***, ***o3***, and major isomer of ***o4*** successfully provided single crystals by the recrystallization from hot solution with slow evaporation, and X-ray single crystal analysis revealed that ***p3***, ***m2***, ***o3***, and major isomer of ***o4*** were the *cis* isomer, and ***o3*** was the *trans* isomer (Fig. 2 and Table S1). These results of observation excellently agreed with the results of above calculation, meaning that the obtained isomers for ***p2***–***p6*** and ***m2***–***m6*** were the *cis* isomers, and that for ***o3*** was the *trans* isomer, due to the energy difference between the isomers. The small energy difference of ***o4*** led to the formation of isomeric mixtures, in which the *cis* isomer was the major product. Although the *cis* isomers are meso compounds, the *trans* isomer of ***o3*** should be a racemic mixture. Indeed, the chiral chromatogram of ***o3*** exhibited two peaks, whereas ***p3***, ***m2***, and the major isomer of ***o4*** showed one peak (Fig. S25–S27). Other TPE macrocycles ***p2***, ***p4***–***p6***, and ***m3***–***m6*** also showed one peak in chiral chromatogram, indicative of the formation of the *trans* isomer for ***o3***, and *cis* isomers for ***p2***–***p6*** and ***m2***–***m6***. These results suggested that the *para*- and *meta*- linkage is advantageous for the formation of *cis* isomer due to the far linking point on the phenyl ring from the central C=C bond, whereas *ortho*- linkage inhibited the formation of *cis* isomer owing to the steric hindrance derived from the vicinity of the linking points.

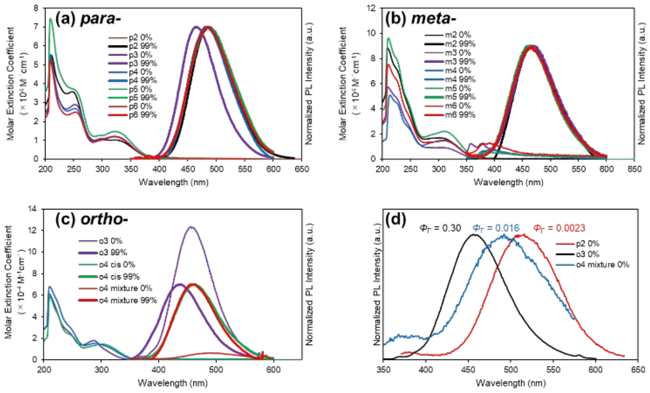


Fig. 3 Absorption (THF, 10 μM) and emission (THF (thin line) and THF/H_2O = 1/99 (*v*/*v*), 10 μM) spectra of (a) ***p2***–***p6***, (b) ***m2***–***m6***, and (c) ***o3***, ***o4*** (cis), and ***o4*** (mixture). The emission spectra were normalized by the spectra in the poor solvent THF/H_2O = 1/99 (*v*/*v*). (d) Normalized emission spectra of ***p2***, ***o3***, and ***o4*** (mixture) in THF (10 μM).

Table 2. Summary of the optical properties.

Molecule	λ_{Abs} (nm)[a]	$\lambda_{Em,Sol}$ (nm)[b]	$\lambda_{Em,Agg}$ (nm)[c]
p2	210, 247, 323	513	486
p3	209, 252, 321	-	466
p4	209, 252, 321	-	483
p5	236, 253, 323	-	488
p6	209, 253, 321	-	485
m2	209, 302	-	469
m3	210, 306	-	467
m4	213, 310	-	463
m5	210, 310	-	464
m6	210, 309	-	465
o3	209, 287	456	440
o4	211, 301	-	462
o4 (mixture)	210, 290	489	460

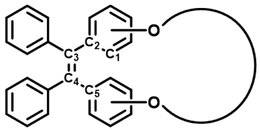
[a] Absorption maxima (THF, 10 μM). [b] Emission maxima in the solution state (THF, 10 μM). [c] Emission maxima in the aggregated state (THF/H_2O = 1/99, 10 μM).

All the obtained TPE macrocycles exhibited strong emission in the aggregated state prepared in a poor solvent (THF/H_2O = 1/99), meaning that these compounds can be potentially regarded as AIEgens (Fig. 3a–c, Table 2) with quantum yields (Φ_F) of 0.02–0.5 (Table S2). The compounds with *para*-linkage provided the emission maxima at around 480~490 nm, whereas those of the compounds with *meta*-linkage were found at around 460~470 nm. This difference probably derived from the electronic effect of the substituted position rather than the steric effect such as distortion of *cis*-stilbene moiety, because the difference of OEG chain length did not influence on the emission maxima. On the other hand, the emission maxima of the compounds with *ortho*-linkage were affected by the OEG chain length, thus the emission maximum of ***o3*** (440 nm) hypsochromically shifted from that of ***o4*** (462 nm), due to the strictly restricted distortion derived from the short OEG chain length. These shift of emission maxima corresponded to the shift of absorption maxima in solution state (Fig. 3a–3c, Table 2), indicating that the substituted position of OEG linkage or the OEG chain length have certain effect on the electronic or steric factors, respectively, in the ground state, as well as in the excited state. In the solid state, all the obtained TPE macrocycles exhibited large hypsochromic shift of 10–60 nm (Fig. S28–S30) with absolute Φ_F of 0.10–0.95 (Table S2), suggesting the phenyl ring rotation in the excited state, leading to more extended π conjugation, is prohibited in the solid state, resulting in the hypsochromic shift of the emission maxima.

Differently from usual TPE derivatives exhibiting AIE properties, ***p*2**, ***o*3**, and ***o*4** (mixture) showed emission in the solution state, whereas ***p*3–*p*6**, ***m*2–*m*6**, and pure ***o*4** showed no emission, which is typical behaviour of AIEgens (Fig. 3d). The emission was intense for ***o*3** (Φ_F = 0.30), while ***p*2** and ***o*4** (mixture) showed low emission (Φ_F = 0.0023 and 0.016, respectively). For ***o*4**, the *trans* isomer seemed to be emissive, because pure ***o*4** (*cis* isomer) was non-emissive whereas the mixture was emissive. The $\lambda_{Em,Sol}$ and Φ_F of these compounds were not differed in various solvents such as ethanol, acetonitrile, and dichloromethane from THF, as shown in Fig. S31 and Table S3 Several groups have reported that the formation of supramolecular complex[39–42] or covalent linkage[49] turns TPE derivatives to be emissive in the solution state due to the restriction of π twist of the central C=C bond in the excited state. From our observation of systematically synthesized TPE macrocycles, too long covalent linkage resulted in a usual AIE property, and a tight fastener is necessary to obtain a TPE derivative exhibiting a strong emission in the solution state to restrict π twist of the central C=C bond in the excited state.

Among the non-emissive TPE macrocycles, ***p*6** and ***m*3–*m*6** showed certain change in ^{1}H NMR spectra after photoirradiation for 1 hour (Fig. S32–S43), indicating a photoreaction took place (Yield, ***p*6**: 20%, ***m*3**: 29%, ***m*4**: 29%, ***m*5**: 35%, ***m*6**: 48%). From the spectra, we did not observe peaks around 2~3 ppm and 9 ppm, which are attributable to dihydrophenanthrene[61] and phenanthrene derivatives,[37] respectively, produced by photocyclization. Therefore, we concluded that the product by photoirradiation should be the *trans* isomer of ***p*6** and ***m*3–*m*6**. This observation suggested that loose fastener cannot suppress the progress of (*E*)-(*Z*) isomerization, and indeed the yield of the isomerization is higher for TPE macrocycles having looser fastener, which is influenced by both the length of OEG chain and the substituted position.

Table 3. The calculated dihedral angle (ϑ_β) for TPE macrocycles at S_0min and S_1min at the B3LYP/6-31G(d) level.



$$\theta_\alpha = \theta(C_1C_2C_3C_4)$$
$$\theta_\beta = \theta(C_2C_3C_4C_5)$$

Molecule	$\vartheta_{\beta,S0}$ (°)[a]	$\vartheta_{\beta,S1}$ (°)[b]	$\Delta\lvert\vartheta_{\beta,S1}-\vartheta_{\beta,S0}\rvert$ (°)
***p*2**	11	42	31
***p*3**	12	45	33
***p*4**	13	55	42
***p*5**	13	51	38
***p*6**	12	53	41
***m*2**	12	84	72
***m*3**	12	90	78
***m*4**	13	91	78
***m*5**	12	96	84
***m*6**	11	95	84
***o*3** (*cis*)	8	66	58
***o*3** (*trans*)	165	143	22
***o*4** (*cis*)	9	72	61
***o*4** (*trans*)	164	135	29

[a] ϑ_β at S_0min. [b] ϑ_β at S_1min.

To obtain a deeper insight into the origin of the strong emission in the solution state of obtained TPE macrocycles, we carried out the theoretical computations to reveal the minimum structure in the excited state (S_1opt) by using time-dependent density functional theory (TD-DFT) method at the B3LYP[58,59]/6-31G(d) level using Gaussian 16,[60] and compared it with the minimum structure in the ground state (S_0opt) computed above. As we previously reported, π twist of the central C=C bond in TPE derivatives is the main pathway of the non-radiative decay in solution state, after excitation at the Franck-Condon (FC) structure.[20] Analogously to our previous observation, at S_1opt. all the obtained TPE macrocycles showed the elongation of the central C=C double bond, indicating the reduction of bond order. On the other hand, the dihedral angle around the central C=C bond in the excited state ($\vartheta_{\beta,S1}$) was affected by the OEG chain length (Table 3), and shorter chain length roughly provided smaller $\vartheta_{\beta,S1}$ (*para*-: 41° (***p*6**) →31° (***p*2**), *meta*-: 84° (***m*6**) →72° (***m*2**), *ortho*-: 29° (***o*4**) → 22° (***o*3**)). In the ground state, the dihedral angle ($\vartheta_{\beta,S0}$) was almost constant (8°–13°) regardless of the substituted position. As a result, the difference of the dihedral angle between the ground and excited state ($\Delta\lvert\vartheta_{\beta,S1}-\vartheta_{\beta,S0}\rvert$) substantially differed dependent on the chain length, and the TPE macrocycles, ***o*3**, ***p*2**, and ***o*4** (*trans*) showed very small $\Delta\lvert\vartheta_{\beta,S1}-\vartheta_{\beta,S0}\rvert$ (***o*3**: 22°, ***o*4** (*trans*): 29°, ***p*2**: 31°). According to the order of Φ_F (***o*3**: 0.30, ***o*4** (mixture): 0.016, ***p*2**: 0.0023), $\Delta\lvert\vartheta_{\beta,S1}-\vartheta_{\beta,S0}\rvert$ decreased. These results indicated that the restriction of π twist of the central C=C bond in the excited state is essential for the emission in the solution state, whereas the π twist usually leads to the access to conical intersection (CI) and subsequent deactivation from the excited state.[52-54] In general, TDDFT/DFT is not an appropriate approach to describe the electronic structures around the CI of S_0 and S_1 states due to difficulty in the SCF convergence, nonetheless, the reciprocally proportional relationship between $\Delta|\vartheta_{\beta,S1}-\vartheta_{\beta,S0}|$ and Φ_F are clearly shown (Figure S44). The *ortho*- linkage significantly diminished the rotation around the central C=C bond in the excited state despite the reduced bond order. Note that the rotation of phenyl rings in the excited state ($\Delta|\vartheta_{\alpha,S1}-\vartheta_{\alpha,S0}|$, Table S4) was mainly affected by the substituted position (*para*-: 24°~30°, *meta*-: 41°~43°, *ortho*-: 11°~19°) rather than the OEG chain length, meaning that the phenyl ring rotation in the excited state have very little effect on the decision of emission.

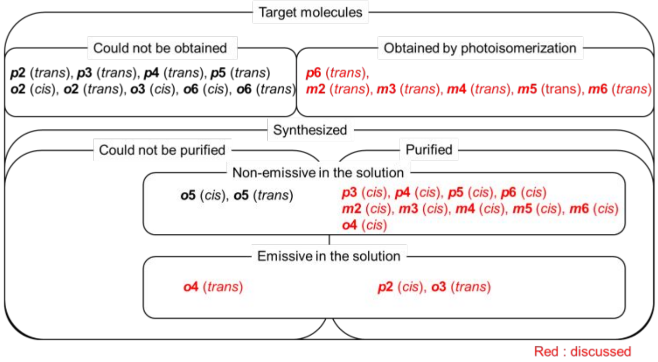


Fig. 4 Summary of synthesis and photoluminescence properties for TPE macrocycles.

Conclusions

In conclusion, we synthesized a series of TPE macrocycles by intramolecular McMurry coupling, in which the vicinal phenyl rings are linked with oligoethylene glycol chain (OEG) (Fig. 4). The substitution at *para*- and *meta*- position provided *cis* isomer of TPE macrocycles, whereas that at *ortho*- position did *trans* isomer in the case of short OEG chain, which was precisely anticipated from total energy of the molecule determined by theoretical computations. All the obtained TPE macrocycles showed strong emission in the aggregated state. The TPE macrocycles with *meta*- linkage exhibited no emission in the solution state, whereas those with *para*- linkage exhibited emission in the solution state in the case of short OEG chain. Moreover, those with *ortho*- linkage exhibited strong emission in the solution state in the case of *trans* isomer, due to the tight fastener. On the other hand, (*E*)-(*Z*) isomerization took place in the case of TPE macrocycles with loose fastener, instead of the strong emission in the solution state. From theoretical computation for these molecules in the excited state, TPE macrocycles showing strong emission in the solution state exhibited smaller difference of the dihedral angle around the central C=C bond between in the ground state and in the excited state, while those showing no emission in the solution state exhibited larger difference. These facts indicate that the tight faster of short OEG chain efficiently restricts π twist of the central C=C bond in the excited state, resulting in the strong emission even in the solution state. As can be seen in our result herein and results reported by others, homogeneous systems can exhibit strong emission of AIEgens without forming an aggregate of the AIEgens. Thus, "aggregation" is only one means to induce strong emission of AIEgens, and the name "aggregation-induced emission" often leads to misunderstanding of this emission phenomenon. The most important factor to induce the emission is obviously restriction of the π twist and distortion of AIEgens in the excited state, which brings about the relaxation pathway to minimum energy conical intersection. Our results presented herein will be a promising basis of rational design for new AIEgens.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors greatly appreciate Prof. Dr. M. Kato, Prof. Dr. A. Kobayashi, and Dr. M. Yoshida for single crystal X-ray diffraction measurement and absolute photoluminescence quantum yield (Φ_F) measurement. We acknowledge financial support from a JSPS KAKENHI Grant Numbers JP18H04495, Asahi Glass Foundation, and JST-PRESTO Grant Number JPMJPR19L3. The HRMS measurement was carried out at the OPEN FACILITY, Hokkaido University Sousei Hall.

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