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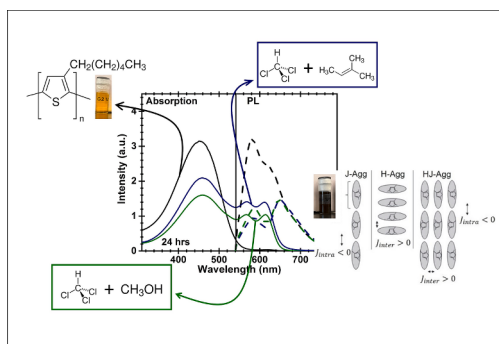
What is the significance of the chloroform stabilizer C₅H₁₀ and its association with MeOH in concentration-dependent polymeric solutions?

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HIGHLIGHTS

- Amylene (C₅H₁₀) limits the lifespan of stabilized chloroform (CHCl₃) as a good solvent.
- Methanol (MeOH) produces similar stabilization of pure CHCl₃ when compared with C₅H₁₀.
- The combination of C₅H₁₀ and MeOH leads to additional routes for controlling interchain interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The understanding of excitonic transitions associated with polymeric aggregates is fundamental, as such transitions have implications on coherence lengths, coherence numbers and inter- and intra-chain binding parameters. In this context, the investigation of efficient solvents and other ways to control polymer aggregate formation is key for their consolidation as materials for new technologies. In this manuscript, we use Poly(3-hexythiophene) (P3HT) as a probe to investigate the significance of amylen (C₅H₁₀) and its association with methanol (MeOH) in both pure and C₅H₁₀-stabilized chloroform (CHCl₃)-based polymeric solutions. Using the intensity ratio between the first and second vibronic transitions of the P3HT H-aggregates formed, values for their exciton bandwidths and interchain interactions are obtained and correlated with the presence of C₅H₁₀ and MeOH as agents determining the CHCl₃ quality.

1. Introduction

The understanding and subsequent characterization of polymeric semiconducting devices has been of heightened interest as the drive for cost effective, high yield and easily processable devices pushes research

interests forward [1–21]. The reproducibility and efficiency of these organic devices are intimately connected with ability of polymers to form films with high-quality aggregates and crystalline domains [1–21]. Recently, new polymers, polymeric structures, and strategies for the development of more efficient organic devices have been explored

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[1–21]. In one hand, Bi et al. [10] achieved 31 % efficiency in organic photovoltaic cells (OPVs) under indoor light using polymer donors with enhanced crystallinities such as series PB3, PB4 and PB5 based on thiadiazole (TDZ), 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDTT) and fluorinated BDT-T (BDT-T-2F). On the other hand, Smeets et al. [11] explored the synthesis of PM6 and D18 to overcome poor reproducibility organic devices' performance, while Wang et al. [15] demonstrated that PQM-Cl-based all-polymer OPV cells enable rarely high JSC and fill factor (FF). Such polymers have been considered as prime candidates for numerous applications (OPVs, photodetectors, charge transport, and solubility/miscibility properties, via rational design of their constituent donor and acceptor building blocks). Benzo[1,2-b:4,5-b']difuran (BDF) based wide bandgap-conjugated polymers, PFCT-2F and PFCT-2Cl, have also been explored to overcome limitations of BDF-based structures due to aggregation properties and unfavorable active layer morphology [14]. In addition, thiazolo-thiazole (TzTz)-thiophene copolymers (PTzBT and PTzBTE) have been explored as alternatives for applications using π -conjugated polymers with higher crystallinity [12]. A series of all-organic dielectric polymer composites have been fabricated by blending the n-type molecular semiconductor 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) with polyetherimide (PEI). Such composites have led to leakage current reductions and improvements in the breakdown strength and energy storage properties at high temperatures [13]. Despite these recent developments, Poly(3-hexothiophene) (P3HT) is still a strong and well-studied player in the field [1,6,27–35].

Polymeric aggregates are traditionally understood as intra- vs inter-chain phenomena [6,8,27–32,36–45]. Casting P3HT as an example, Fig. 1 shows two traditional types of aggregates classified as H-aggregates (side-by-side stacking of neighboring chains) and J-aggregates (tip-to-tail stacking of neighboring chains). Fig. 1 also displays the so-called HJ-aggregate, which is an interplay between H- and J-aggregate made possible through variation of the polymers inter (J_{inter}) and intra (J_{intra}) chain coulombic coupling [6,8,27–32,36–45]. Each of these aggregates possesses unique optoelectronic properties, including well-defined photoluminescence (PL) and absorption (Abs) spectral signatures [27–32,39–41,44–46]. In fact, variations in excitonic coupling in the development of each aggregate formation results in varying spectral

signatures. For example, the formation of J-aggregates is a result of negative excitonic coupling with $J_{\text{intra}} < 0$ and $J_{\text{inter}} = 0$ which subsequently allows for 0–0 emission at low temperatures. Alternatively, H-aggregate formations are a result of positive excitonic coupling with $J_{\text{inter}} > 0$ and $J_{\text{intra}} = 0$ which leads to a forbidden 0–0 emission at low temperatures. In HJ-aggregates ($J_{\text{intra}} \neq 0$ and $J_{\text{inter}} \neq 0$), for example, there is a competition between intra- and inter-chain interactions [39–41,44–46].

Theoretical developments demonstrate that J-, H-, and HJ-aggregate PL and Abs signatures are altered with variation of J_{inter} and J_{intra} [39–41,44–46]. In one hand, the ratio of the PL peak intensity of the 0–0 and 0–1 transitions ($I_{\text{PL}}^{0-0}/I_{\text{PL}}^{0-1}$) is used to determine the coherence number (N_{coh}) and length (l_0). On the other hand, the ratio of the Abs first (A_1) and second (A_2) vibronic progressions (A_1/A_2) and of the third (A_3) vibronic progression and A_2 (A_3/A_2) are both < 1 (> 1) for H- (J- and HJ-) aggregates. The H- (J- and HJ-) aggregate A_1/A_2 ratio decreases (increases) with increasing J_{inter} (J_{intra}), while the opposite behavior is observed for the A_3/A_2 ratio. In addition, the H- (J- and HJ-) aggregate $I_{\text{PL}}^{0-0}/I_{\text{PL}}^{0-1}$ ratio increases (decreases) with increasing temperature. Altogether, these ratios are rather convenient to determine the different types of aggregates as well as to evaluate quality and efficiency of solvents to form and control such aggregates through the fine-tuning of both J_{inter} and J_{intra} [39–41,44–46].

Several strategies have been proposed to controllably aggregate a variety of polymers [4,6,8,10–27,30–32,47–62]. All of them exploring different solvents and parameters such as molecular weights, synthetic methods, external stimuli (e.g. pressure and temperature), and concentration [4,6,8,10–27,30–32,47–62]. Notably, P3HT has been a model polymer in such studies. Reichmanis and co-workers photoinduced aggregation of P3HT in solution using continuous UV light [60], and more recently Barbosa Neto et al. [61] demonstrated a new photoinduced approach using pulsed visible light to generate highly ordered P3HT J- and HJ-aggregate structures. In addition, Panzer and co-workers [30] utilized temperature to investigate phase transitions and the controllable formation of distinct P3HT H-aggregates in tetrahydrofuran (THF) solutions. In terms of solvents, chloroform (CHCl_3) stabilized with amylene (C_5H_{10}) has been a champion choice as it is widely considered as an excellent and versatile solvent for several polymers, including P3HT. Pure CHCl_3 is usually avoided since it tends to degrade more easily than stabilized ones.

In this work, we use P3HT solutions as probes (backed-up by theory, as discussed above) to investigate in greater detail the role of stabilizers in CHCl_3 . Most often, studies using CHCl_3 neglect the effects of stabilizers in the aggregation process. Our preliminary results, however, showed that even though stabilizers are used in very small amounts, and even though they retard CHCl_3 degradation, they also render the stabilized CHCl_3 a worse solvent when compared with the pure CHCl_3 . Such results led us to investigate more deeply the effect of C_5H_{10} in the effectiveness of stabilized CHCl_3 as a good solvent. We also explored methanol MeOH, as well as its combination with C_5H_{10} as alternative CHCl_3 stabilization routes. We show the following main results: (1) C_5H_{10} limits the lifespan of stabilized CHCl_3 as a good solvent, leading to aggregate formation in 24 h after solution preparation; (2) MeOH produces similar stabilization of pure CHCl_3 when compared with C_5H_{10} ; and (3) the combination of both C_5H_{10} and MeOH opens up additional routes for controlling the J_{inter} magnitude, as C_5H_{10} limits the MeOH action in CHCl_3 .

2. Experimental details

2.1. Materials

All materials and reagents were used as received. Poly(3-hexothiophene) (P3HT) (>98 % head-to-tail regioregular, average Mn 54 000–75 000, 99.995 %; Mn/Mw ≤ 2.5 , electronic graded from Sigma

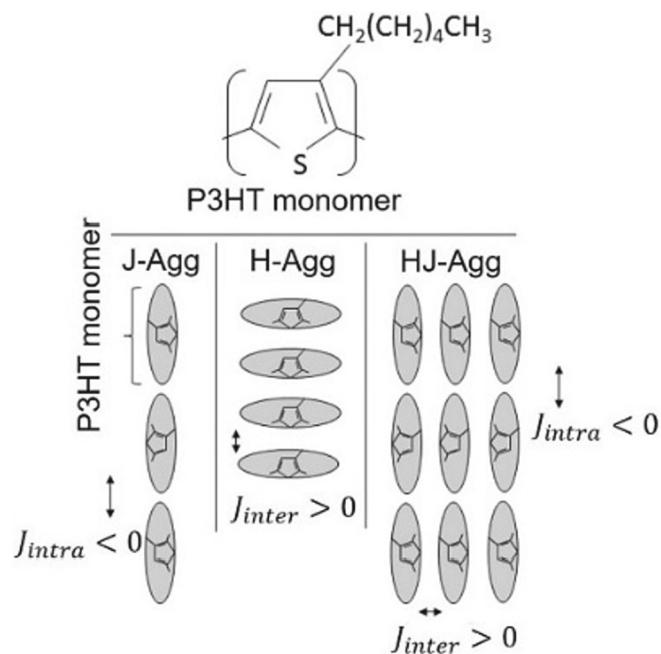


Fig. 1. (a) The P3HT repeat monomer with schematic representations of J-, H-, and HJ- aggregates. The coupling constants J_{inter} and J_{intra} are shown for clarity.

Aldrich) was dissolved in both chloroform (CHCl_3) stabilized with amylene (C_5H_{10}) (Sigma-Aldrich, containing 100–200 ppm amylenes as stabilizer; $\geq 99.5\%$) and pure CHCl_3 (Sigma-Aldrich; $\geq 99.9\%$) at an initial concentration of 0.45 mg/mL. This original solution was then placed on a hot plate (Curtin Matheson 267–914) at 45°C for 45 min. A magnetic stirrer bar was placed inside the solution vial in order to achieve a better dissolving process. The original solutions were then further diluted in order to obtain the two values of concentration used here: 0.005 mg/mL and 0.05 mg/mL. The diluted solutions were then stirred on a hot plate at 45°C for additional 45 min to achieve isolated-chain (amorphous chains) state. The solutions were then stored in a dark box to avoid photo-degradation.

2.2. Absorption

Absorption spectra are obtained using an Agilent Cary 50 spectrophotometer running dual-beam mode. All measurements are performed in ambient conditions. Solutions are always transferred from vials to a glass cuvette upon measurements.

2.3. Photoluminescence

Photoluminescence spectra are collected through an in-house designed setup utilizing an Andor iDus 401 series model DV401A CCD with Shamrock model 303i spectroscopy containing 300-line-per-millimeter grating. The CCD and spectroscopy are controlled via Andor Solis computer interface software. The main laser source is an OPLS (Optically Pumped Semiconductor Diode) Sapphire 532–50 CW CDRH laser, which produces vertically polarized light at 532 nm. All measurements are performed in ambient conditions. Solutions are always transferred from vials to a glass cuvette upon measurements.

3. Results and discussion

Two distinct P3HT solutions were prepared at concentrations 0.005 mg/mL (from now on low concentration) and 0.05 mg/mL (from now on high concentration) using as solvents, pure CHCl_3 (from now on CHCl_3), CHCl_3 stabilized with C_5H_{10} (from now on $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$), and CHCl_3 and $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ mixed with distinct MeOH aliquots (from now on $\text{CHCl}_3 + \text{MeOH}$ and $\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$, respectively). All the PL and Abs measurements were performed just after solution preparation (i.e. 0 hrs) and 24 h later. In overall, the amount of C_5H_{10} in the solutions is about 10^6 less than the amount of MeOH added.

3.1. P3HT/ CHCl_3 , P3HT/ $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ and P3HT/ $\text{CHCl}_3 + \text{MeOH}$ solutions at low and high concentrations

Fig. 2 shows representative Abs and PL spectra from P3HT/ CHCl_3 and P3HT/ $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ solutions at concentration 0.05 mg/mL measured at 0 hrs and 24 h later. As observed in Fig. 2(a), at 0 hrs both Abs (solid curves) and PL (dashed curves) spectra from both solutions exhibit clear signatures of isolated chains (i.e. more disordered chains forming intrachain states) with no signs of aggregate formation [27–35,60–62]. However, as shown in Fig. 2(b), the same solutions measured 24 hrs later exhibit completely distinct results: the P3HT/ CHCl_3 solution (black solid and dashed curves) still exhibits spectral signatures that are typical from isolated chains [27–35,60–62]; in contrast the P3HT/ $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ solution (navy solid and dashed curves) shows clear evidence of aggregate formation with well-structured vibronic progressions (first (A_1) and second (A_2) progressions, respectively). As seen in Table 1 the A_1/A_2 ratio is 0.96, and this value along with the well-structured ordered phase in the Abs spectrum suggest the establishment of weakly interacting H-aggregate states [30,31,39–41,44–46,60–62]. Due to the weakly interacting character of such H-aggregates, we understand that both the inner filter (IF) and the self-absorption (SA) phenomena are taking place in the PL spectra [63], and the overall behavior agrees well with results by Panzer and co-workers [30] that in their temperature-related studies, also

Table 1

Values for the A_1/A_2 ratio, A_3/A_2 ratio, exciton bandwidth (W) and interchain interaction (J_{inter}) for different solutions and concentrations.

P3HT/ CHCl_3 solutions: low (high) concentrations				
MeOH aliquots (μL)	A_1/A_2	A_3/A_2	W(meV)	J_{inter} (meV)
0	–	–	–	–
90	0.95 (0.99)	0 (0)	13 (0.5)	3 (0.14)
270	0.95 (0.77)	0.85 (0.92)	13 (71)	3 (18)
450	0.89 (0.72)	0.85 (0.92)	32 (90)	8 (22)

P3HT/ $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ solutions: low (high) concentrations				
MeOH aliquots (μL)	A_1/A_2	A_3/A_2	W(meV)	J_{inter} (meV)
0	0.85 (0.96)	0 (0)	44 (10)	11 (2)
90	0.93 (0.96)	0.82 (0.80)	21 (10)	5 (2)
270	0.93 (0.91)	0.82 (0.80)	21 (26)	5 (7)
450	0.99 (0.85)	0.72 (0.84)	2 (45)	0.57 (11)

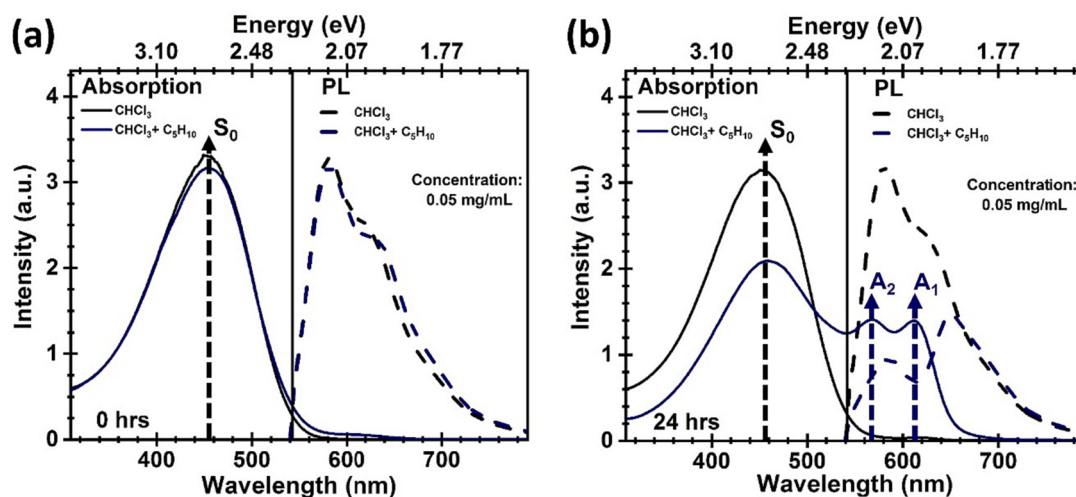


Fig. 2. Absorption (Abs) (solid curves) and Photoluminescence (PL) (dashed curves) spectra for P3HT/ CHCl_3 (black curves) and P3HT/ $\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ (navy curves) high concentration solutions at 0 hrs (a), and 24 hrs (b). The center peaks for the vibronic progressions in (b) are $A_1 = 613$ nm and $A_2 = 568$ nm. **All the figures:** the center peak for the isolated chains (i.e. amorphous phase) is $S_0 = 455$ nm.

observed H-aggregate formation in P3HT/THF solutions. It is important to comment that no significant evidence of aggregation is observed between 0 and 24 hrs. Therefore, within this time interval, both P3HT/CHCl₃ and P3HT/CHCl₃ + C₅H₁₀ are equally good for applications that require solutions with isolated chain properties. After such a time interval, it becomes noticeable that the stabilization of CHCl₃ comes with a cost: the P3HT/CHCl₃ + C₅H₁₀ solutions shows clear signs of crystallization (ordered-phase) and PL self-absorption, while the P3HT/CHCl₃ solutions remain amorphous.

To better understand the role of C₅H₁₀ as a stabilizer and aggregation agent, MeOH was used as a stabilizer for CHCl₃ and as an agent for CHCl₃ + C₅H₁₀ quality tuning. As shown in Fig. 3, the P3HT/CHCl₃ + MeOH (90 μ L) solution at 0.05 mg/mL, in which 90 μ L of MeOH is added to CHCl₃, leads to similar aggregate formation when compared to P3HT/CHCl₃ + C₅H₁₀ ($A_1/A_2 = 0.96$; Fig. 2(b)). The A_1/A_2 ratio is 0.99 (see Table 1), indicating similar weakly interacting H-aggregate formation with a larger predominance of the isolated chain properties within the aggregates [30,31,39–41,44–46,60–62]. Once again, the PL shows clear evidence of both IF and SA phenomena [63], and the overall behavior agrees well with the results observed for the P3HT/CHCl₃ + C₅H₁₀ solution. Although Fig. 3 shows PL and Abs spectra for solutions measured 24 hrs after preparation, the aggregate formation in P3HT/CHCl₃ + MeOH solutions occurs instantaneously and remains unchanged over 24 hrs. In spite of the distinct chemical composition observed for C₅H₁₀ and MeOH, no signs of PL and Abs blue- or red-shift is observed (i.e. no signs of solvatochromism or phase transitions are present) [30,31,39–41,44–46,60–62].

PL and Abs measurements of solutions at low concentration (0.005 mg/mL) were also performed, as shown in Fig. 4(a) (CHCl₃-based solutions) and (b) (CHCl₃ + C₅H₁₀-based solutions). The spectra are reproducible and were taken 24 hrs after solution preparation. Once again, no signs of aggregation between 0 and 24 hrs, for the CHCl₃ and CHCl₃ + C₅H₁₀ solutions. After 24 hrs, however, aggregate formation in CHCl₃ + C₅H₁₀ similar to those observed for high concentration solutions also occurs. This indicates that aggregate formation over time is majorly driven by C₅H₁₀ and not by the concentration of the solution. As

discussed below, the concentration will not influence the type of aggregate formed (H-aggregate) but will change their exciton bandwidths and J_{inter} , which might have a direct influence in the performance of a device. In addition, the study at low concentration is advantageous because it eliminates the previously mentioned IF and SA effects [63] and evaluate, therefore, the true emission profile of the emerging aggregates. Also, even at lower concentrations, solutions with MeOH aggregate instantaneously and remains unchanged over 24 hrs. The amount of MeOH is also varied, and now aliquots of 90 μ L and 270 μ L are added to both P3HT/CHCl₃ + MeOH (Fig. 4(a)) and P3HT/CHCl₃ + C₅H₁₀ + MeOH (Fig. 4(b)) solutions.

Fig. 4(a) shows the low concentration PL and Abs spectra from solutions of P3HT/CHCl₃, P3HT/CHCl₃ + MeOH (90 μ L) and P3HT/CHCl₃ + MeOH (270 μ L), in which 270 μ L of MeOH is added to CHCl₃. When compared to the results in Fig. 3 (see olive solid curve), it is seen that the same H-aggregates structuration are produced and the difference between P3HT/CHCl₃ + MeOH (90 μ L) and P3HT/CHCl₃ + MeOH (270 μ L) seems to be the amount of aggregates formed. Indeed the A_1/A_2 ratio, see Table 1, is 0.95 for both P3HT/CHCl₃ + MeOH (90 μ L) and P3HT/CHCl₃ + MeOH (270 μ L). When compared with the A_1/A_2 ratio of 0.99 found for the high concentration P3HT/CHCl₃ + MeOH (90 μ L) solutions (see Fig. 3), the A_1/A_2 ratio of 0.95 confirms that variations in concentration affect the J_{inter} magnitudes. The presence of an isosbestic point around 500 nm suggests that the decrease in the number of amorphous chains is equal to the number of aggregates formed. In other words, at low concentrations, different aliquots of MeOH only change the amounts of aggregates formed but not their properties. No effects associated with solvatochromism are observed neither with relation to the high concentration P3HT/CHCl₃ + MeOH (90 μ L) case (Fig. 3) nor after changing the MeOH aliquots. This indicates that, although worsening the CHCl₃ quality as a good solvent, the addition of MeOH is not substantially changing the CHCl₃ polarity. It is noteworthy that the PL spectrum no longer shows evidences for IF and SA effects and the PL from isolated chains (black dashed curve) and from the aggregates (navy and olive dashed curves) are rather similar, confirming that the H-aggregates formed are in the weakly coupled regime, where their emission are dominated by chain-backbones in the H-aggregate structure [30,31,39–41,44–46].

Fig. 4(b) shows the low concentration PL and Abs spectra from P3HT/CHCl₃ + C₅H₁₀ at 0hrs, P3HT/CHCl₃ + C₅H₁₀ at 24 hrs, P3HT/CHCl₃ + C₅H₁₀ + MeOH (90 μ L) and P3HT/CHCl₃ + C₅H₁₀ + MeOH (270 μ L) solutions. This time the MeOH aliquots were added to the stabilized CHCl₃ (i.e. CHCl₃ + C₅H₁₀). In one hand, the PL spectra show no signs of IF and SA phenomena and follow the profile observed for the isolated chains, in which the aggregates' emission are dominated by the chain-backbones in the H-aggregate structure (weakly coupled regime). The Abs spectra, on the other hand, show that the vibronic progressions A_1 and A_2 are blueshifted in energy (decrease in wavelength) for the low concentration P3HT/CHCl₃ + C₅H₁₀ at 24hrs solution (see gray-solid curve in Fig. 4(b)) when compared against its high concentration P3HT/CHCl₃ + C₅H₁₀ at 24hrs counterpart (see the navy solid curve in Fig. 3), which in turn possess the same A_1 and A_2 peak positions observed for the high concentration P3HT/CHCl₃ + MeOH (90 μ L) case (Fig. 3). By recalling that no solvatochromism is observed for the low concentration P3HT/CHCl₃ + MeOH (90 μ L and 270 μ L) cases, and since the amount of C₅H₁₀ in the solutions is the same, this non-solvatochromic shift must be associated with the changes in concentration.

Interestingly, the Abs spectra from both low concentration P3HT/CHCl₃ + C₅H₁₀ + MeOH (90 μ L) and P3HT/CHCl₃ + C₅H₁₀ + MeOH (270 μ L) (navy and olive solid curves in Fig. 4(b)) show that the blueshift observed for the vibronic progressions A_1 and A_2 decrease in comparison with the peak positions for the low concentration P3HT/CHCl₃ + C₅H₁₀ at 24hrs solution (grey solid curve in Fig. 4(b)). This is clear evidence of solvatochromism, in which, contrarily to what is observed for the CHCl₃ + MeOH cases, the polarity of the CHCl₃ + C₅H₁₀ solvent is

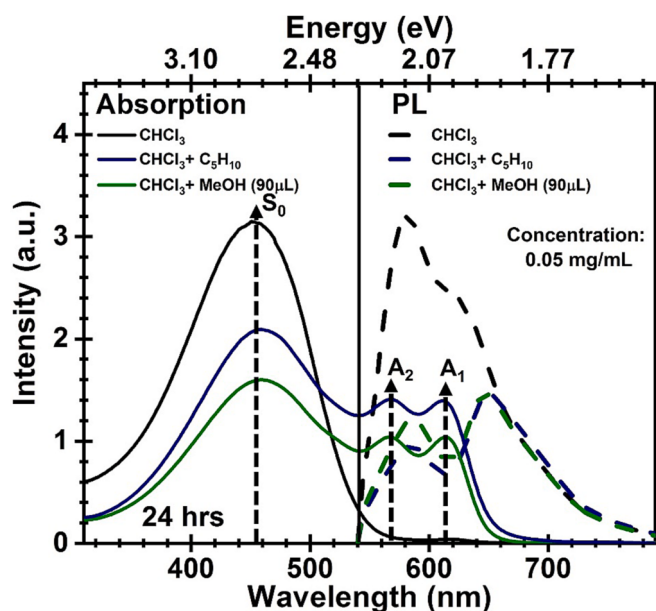


Fig. 3. Absorption (Abs) (solid curves) and Photoluminescence (PL) (dashed curves) spectra for P3HT/CHCl₃ (black curves), P3HT/CHCl₃ + C₅H₁₀ (navy curves), and P3HT/CHCl₃ + MeOH (90 μ L) (olive curves) solutions at 24 hrs. The center peaks for the vibronic progressions in (b) are $A_1 = 613$ nm and $A_2 = 568$ nm. The center peak for the isolated chains (i.e. amorphous phase) is $S_0 = 455$ nm.

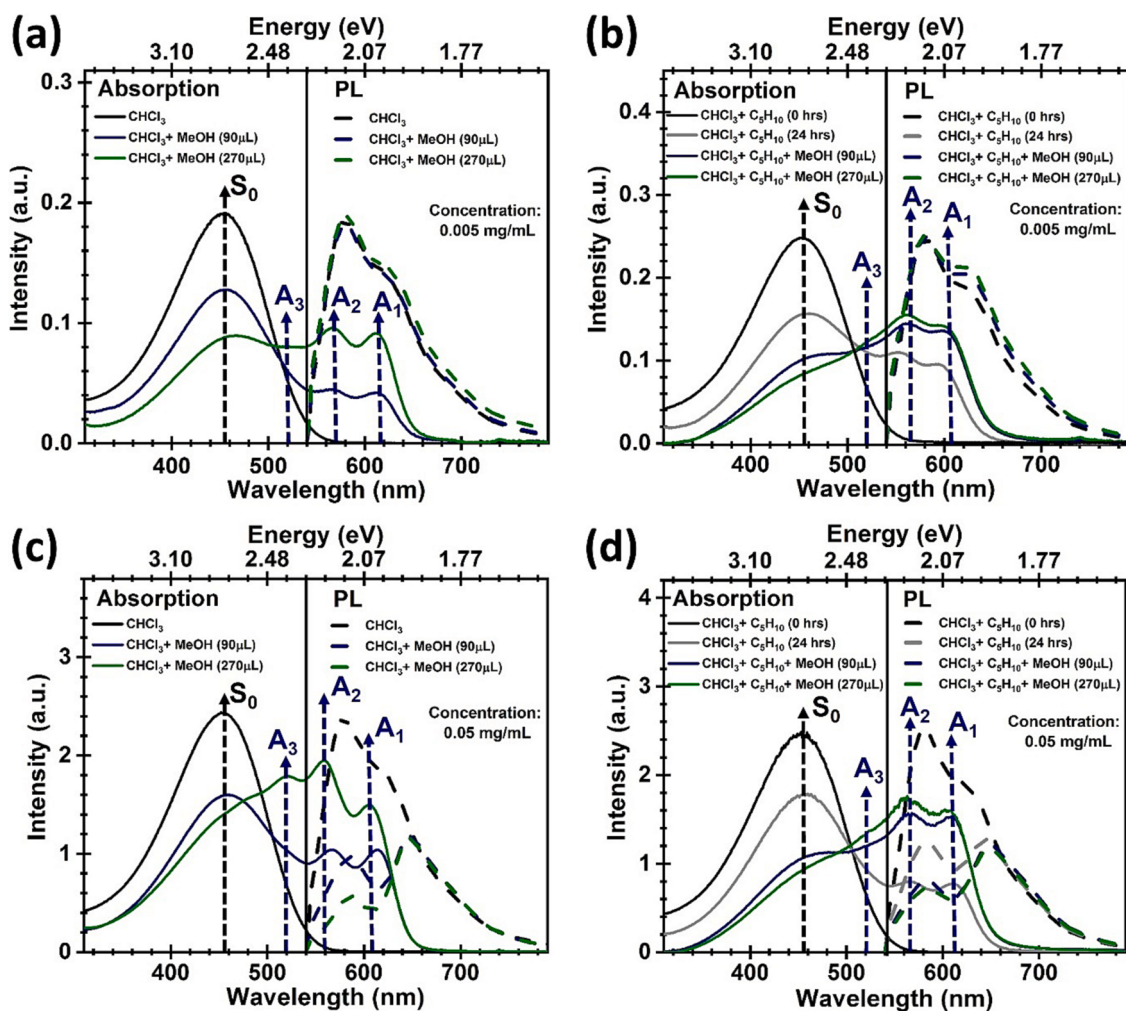


Fig. 4. Absorption (Abs) (solid curves) and Photoluminescence (PL) (dashed curves) spectra for P3HT/CHCl₃ (black curves), P3HT/CHCl₃ + MeOH (90 μ L) (navy curves), and P3HT/CHCl₃ + MeOH (270 μ L) (olive curves) solutions at 24 hrs: (a) concentration 0.005 mg/mL, where the vibronic progressions are located at A₁ = 613 nm, A₂ = 568 nm, and A₃ = 521 nm for both navy and olive curves (A₃ is not observed for the navy curve), and (c) concentration 0.05 mg/mL, where the vibronic progressions are located at A₁ = 606 nm, A₂ = 559 nm, and A₃ = 521 nm for the olive curve, and A₁ = 613 nm and A₂ = 568 nm for the navy curve (A₃ is not observed for the navy curve). Absorption (Abs) (solid curves) and Photoluminescence (PL) (dashed curves) spectra for P3HT/CHCl₃ + C₅H₁₀ at 0 hrs (black curves), P3HT/CHCl₃ + C₅H₁₀ (gray curves), P3HT/CHCl₃ + C₅H₁₀ + MeOH (90 μ L) (navy curves), and P3HT/CHCl₃ + C₅H₁₀ + MeOH (270 μ L) (olive curves) solutions at 24 hrs: (b) concentration 0.005 mg/mL, where the vibronic progressions are located at A₁ = 603 nm, A₂ = 562 nm, and A₃ = 521 nm for the olive and navy curves, and A₁ = 595 nm and A₂ = 553 nm for the gray curve (A₃ is not observed for the gray curve), and (d) concentration 0.05 mg/mL, where the vibronic progressions are located at A₁ = 613 nm, A₂ = 568 nm, and A₃ = 521 nm for all the curves (A₃ is not observed for the gray curve). **All the figures:** the center peak for the isolated chains (i.e. amorphous phase) is S₀ = 455 nm.

modified upon the addition of MeOH aliquots. This can be explained by the fact that C₅H₁₀ has several sites for establishing hydrogen bonds with the OH group in MeOH, which is an electronegative group. Usually, the hydrogen bonding capacity along with the dielectric constant are the most important properties in a solvent, being directly associated with the aforementioned solvatochromic effect. In addition, for the P3HT/CHCl₃ + C₅H₁₀ + MeOH (90 μ L) and P3HT/CHCl₃ + C₅H₁₀ + MeOH (270 μ L) low concentration solutions, the amount of H-aggregates produced are the same, in contrast with the low concentration P3HT/CHCl₃ + MeOH (90 μ L) and P3HT/CHCl₃ + MeOH (270 μ L) cases reported in Fig. 4(a), in which the increase of MeOH aliquot leads to the increase in the amount of aggregates. This is further evidence that the presence of C₅H₁₀ do influence the capacity for aggregate formation. The Abs spectra in Fig. 4(b) is less structured than the spectra shown in Fig. 4(a), indicating less planar aggregates [30,31,60–62] with a A₁/A₂ ratio of 0.93 (see Table 1), which is still in agreement with the weakly coupled aggregate regime. There is no longer a common isosbestic point but the crossing point in the PL and Abs from the different solutions are very

close to each other suggesting that, although not one to one, most of amorphous chains are transitioning to the ordered aggregated phase. In other words, C₅H₁₀ seems to harden the formation of more planar aggregates.

As seen in Fig. 4(c) (CHCl₃-based solutions) and (d) (CHCl₃ + C₅H₁₀-based solutions), the high concentration regime (0.05 mg/mL), shows the expected concentration-related enhancements in the overall Abs and PL intensities but such enhancements come with other interesting scenarios. In such regime, there is no spectral energy shifts observed for solutions prepared with CHCl₃ + C₅H₁₀ even after MeOH addition, see Fig. 4(d). In other words, it seems that the increase in concentration renders the solvatochromic effect in Fig. 4(b) negligible. Once again, for the P3HT/CHCl₃ + C₅H₁₀ + MeOH (90 μ L) and P3HT/CHCl₃ + C₅H₁₀ + MeOH (270 μ L) high concentration solutions, the amount of H-aggregates produced are essentially the same, in contrast with the high concentration P3HT/CHCl₃ + MeOH (90 μ L) and P3HT/CHCl₃ + MeOH (270 μ L) cases reported in Fig. 4(c), in which the increase (decrease) of MeOH aliquot is associated with the increase (decrease) in the amount of

aggregates. The results replicate those from low concentration samples, which is an indication that even at higher concentrations, the presence of C_5H_{10} renders MeOH ineffective to influence the capacity for aggregate formation. It is also noticeable that in such C_5H_{10} + MeOH solutions, MeOH loses effectiveness in controlling J_{inter} (see the similar A_1/A_2 ratios for both low and high concentrations in Table 1). Indeed, as shown in Fig. 4(d), the Abs spectra shows that no significant differences are observed with changing the MeOH aliquots, except for a slight increase in the vibronic progression A_2 intensity, and for the rise of a weak vibronic progression A_3 in the solution where 270 μ L of MeOH is added. The A_1/A_2 ratio is 0.91, while the A_3/A_2 ratio is 0.80 (see Table 1), which indicate that in this case the J_{inter} is essentially unchanged. Similarly to the low concentration case (Fig. 4(b)), there is no common isosbestic point but the crossing point in the Abs from the different

solutions are very close to each other. The conclusion is the same as before: although not one to one, most of amorphous chains are transitioning to the ordered aggregated phase.

An energy blueshift of about 0.14 eV is observed in the Abs spectra with increasing the amount of MeOH from 90 to 270 μ L in solutions prepared with $CHCl_3$ (see Fig. 4(c)). Since no solvatochromism is observed at low concentrations (see Fig. 4(a)), this blueshift effect together with the enhanced structuration of the vibronic progressions suggest that the combination of a higher concentration with a higher amount of MeOH is inducing a tighter packing and enhanced H-aggregate behavior, which is consistent with modifications in the J_{inter} magnitude. Such effect has been observed in Lutein H-aggregates [64,65], and it is not strongly observed in C_5H_{10} + MeOH solutions. As expected, both the IF and SA effects are once again observed in the PL

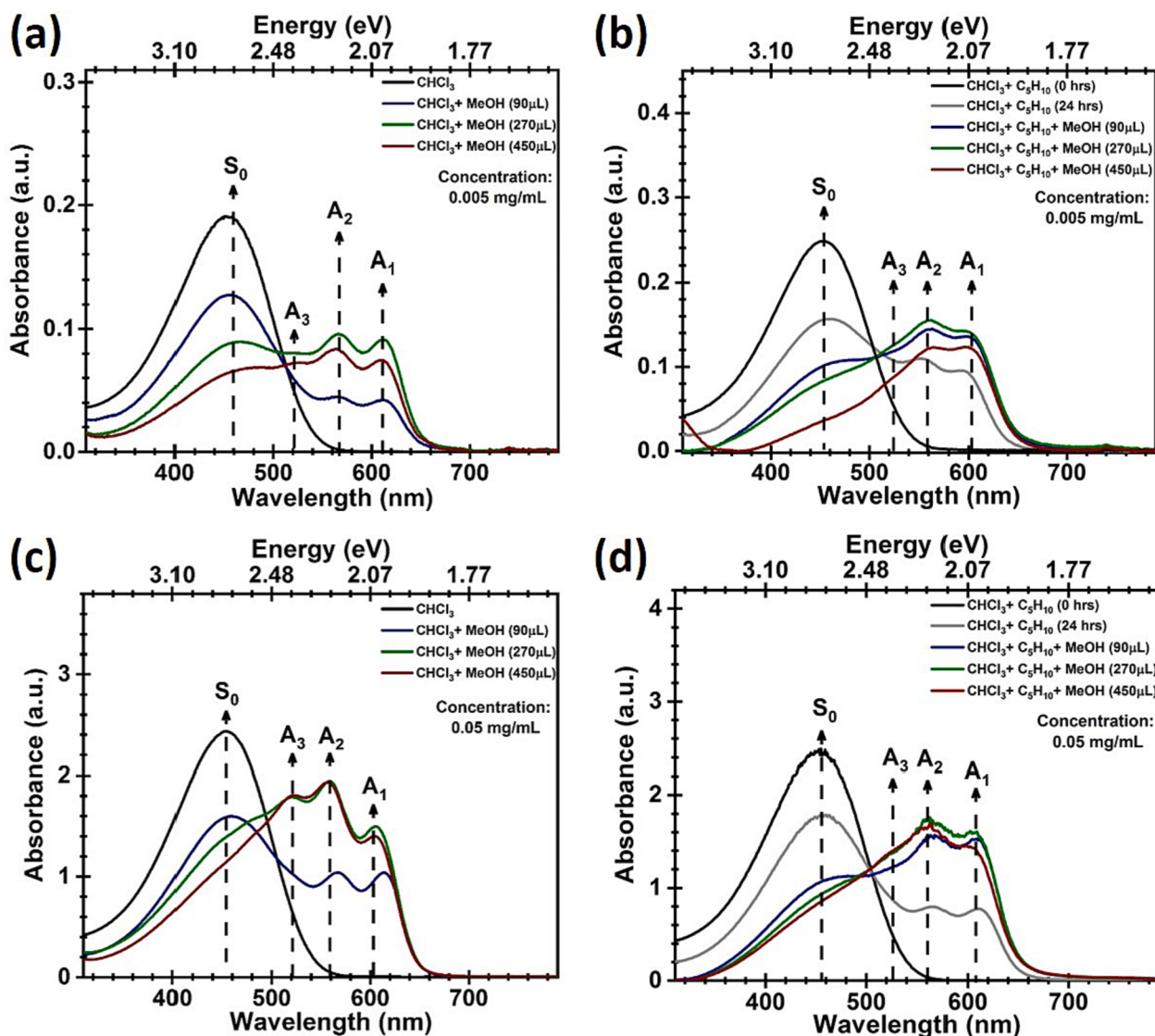


Fig. 5. Absorption (Abs) (solid curves) spectra for P3HT/ $CHCl_3$ (black curves), P3HT/ $CHCl_3$ + MeOH (90 μ L) (navy curves), P3HT/ $CHCl_3$ + MeOH (270 μ L) (olive curves), and P3HT/ $CHCl_3$ + MeOH (450 μ L) (wine curves) solutions at 24 hrs: (a) concentration 0.005 mg/mL, where the vibronic progressions are located at A_1 = 613 nm, A_2 = 568 nm, and A_3 = 521 nm for all the curves (A_3 is not observed for the navy curve), and (c) concentration 0.05 mg/mL, where the vibronic progressions are located at A_1 = 606 nm, A_2 = 559 nm, and A_3 = 521 nm for the olive and wine curves, and A_1 = 613 nm and A_2 = 568 nm for the navy curve (A_3 is not observed for the navy curve). Absorption (Abs) (solid curves) spectra for P3HT/ $CHCl_3$ + C_5H_{10} at 0 hrs (black curves), P3HT/ $CHCl_3$ + C_5H_{10} (gray curves), P3HT/ $CHCl_3$ + C_5H_{10} + MeOH (90 μ L) (navy curves), P3HT/ $CHCl_3$ + C_5H_{10} + MeOH (270 μ L) (olive curves), and P3HT/ $CHCl_3$ + C_5H_{10} + MeOH (450 μ L) (wine curves) solutions at 24 hrs: (b) concentration 0.005 mg/mL, where the vibronic progressions are located at A_1 = 603 nm, A_2 = 562 nm, and A_3 = 521 nm for the navy, olive and wine curves, and A_1 = 595 nm and A_2 = 553 nm for the gray curve (A_3 is not observed for the gray curve), and (d) concentration 0.05 mg/mL, where the vibronic progressions are located at A_1 = 613 nm, A_2 = 568 nm, and A_3 = 521 nm for all the curves (A_3 is not observed for the gray curve). All the figures: the center peak for the isolated chains (i.e. amorphous phase) is S_0 = 455 nm.

but this time, the Abs spectra show that the addition of MeOH is changing the amount of aggregates produced as well as their vibronic progressions' intensities (i.e. J_{inter} is dependent on the MeOH aliquots in the absence of C_5H_{10}). In the case of $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ solutions (Fig. 4(c)), it seems that the H-aggregates are not only more structured but also more efficiently formed with increasing the amount of MeOH from 90 to 270 μL . In addition, the Abs profile from the $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (270 μL) solution shows a third vibronic progression A_3 , and now the A_1/A_2 ratio is 0.77, while the A_3/A_2 ratio is 0.92 (see Table 1), which endorses the H-aggregate character of the ordered phase and that modifications in the J_{inter} magnitude are taking place indeed [30,31,39–41,44–46,60–62]. Although there is a clear isosbestic point for the $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (90 μL) solution, in the case of the $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (270 μL) the shift observed in the Abs crossing point suggest that instead of an equal number of amorphous chains being converted into aggregates in the ordered phase, it might be happening a joint effect of aggregate formation with different planarization as well as distinct planarization of isolated chain in the amorphous phase, which are usually coiled or irregular when fully dissolved in a good solvent such as CHCl_3 [30,31,62]. This type of effect has been suggested in a study by Scharsich and collaborators [31], and it seems to be reduced by the presence of C_5H_{10} in CHCl_3 .

3.2. P3HT as a probe to understand C_5H_{10} and MeOH as agents to control J_{inter} and exciton bandwidths (W)

Fig. 5(a)–(d) focus on a complementary but deeper analysis of representative Abs spectra, at both the low and high concentration regimes, discussed throughout the manuscript. This time, three distinct MeOH aliquots are added to pure (CHCl_3) and stabilized ($\text{CHCl}_3 + \text{C}_5\text{H}_{10}$) chloroform: 90, 270 and 450 μL . In all the figures, S_0 stands for the absorption observed for isolated chains (i.e. amorphous phase), and A_i for $i = 1, 2, 3$ stand for the vibronic progressions. In the weakly coupling regime the ratio A_1/A_2 of vibronic progressions in H-aggregates is approximated by [30,31,39–41,44–46,60–62]:

$$\frac{A_1}{A_2} \approx \left(\frac{1 - 0.24 \left(\frac{W}{E_p} \right)}{1 + 0.073 \left(\frac{W}{E_p} \right)} \right)^2, \quad (1)$$

where W is the exciton bandwidth and E_p is the energy of the main intramolecular vibration coupled to the electronic transition (i.e. the $\text{C}=\text{C}$ symmetric stretch at 0.18 eV in the case of P3HT) [30,31,39–41,44–46,60–62]. Using Equation (1), the experimental values for A_1/A_2 , and $E_p = 0.18$ eV, the exciton bandwidth W can be obtained. The exciton bandwidth is 4 times the J_{inter} magnitude ($W = 4|J_{\text{inter}}|$), and therefore, J_{inter} can be obtained as well. The weak excitonic coupling regime (i.e. the weakly coupling or polymer regime) occurs whenever $W < 0.26$ eV [39–41,44–46]. In addition, W is associated with the conjugation length and intrachain order: an increase in conjugation and order leads to a decrease in W . Solving Equation (1) for W results in:

$$W = 4|J_{\text{inter}}| \approx E_p \left(\frac{1 - \left(\frac{A_1}{A_2} \right)^{1/2}}{0.24 + 0.073 \left(\frac{A_1}{A_2} \right)^{1/2}} \right) \quad (2)$$

Next, a discussion using Equations (1) and (2) is addressed for the several solutions considered above.

Fig. 5(a) shows representative Abs spectra for solutions (concentration 0.005 mg/mL) of $\text{P3HT}/\text{CHCl}_3$ (black solid curve), $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (90 μL) (navy solid curve), $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (270 μL) (olive solid curve), and $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (450 μL) (wine solid curve). At this concentration, the A_1/A_2 ratios are 0.95, 0.95, and 0.89 for the solutions with 90, 270, and 450 μL of MeOH added, respectively (see

Table 1). The vibronic progression A_3 starts to show up for the solutions where 270 and 450 μL are added, and both A_3/A_2 ratios are the same: 0.85. As summarized in Table 1, $W = 13$ meV and $J_{\text{inter}} = 3$ meV for the solutions where 90 and 270 μL are added, while $W = 32$ meV and $J_{\text{inter}} = 8$ meV for the solutions where 450 μL is added. The increase in the values of W and J_{inter} suggest that the conjugation lengths are decreasing (i.e. lowering the crystalline quality of the aggregate) [30,31,60–62]. As mentioned previously, the isosbestic point observed for the solutions where 90 and 270 μL of MeOH are added suggests a one to one conversion of isolated chains into H-aggregates. This is not the case for the $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (450 μL) solution, indicating that the extra amount of MeOH added (67 % more with relation to the 270 μL aliquot) is likely affecting the conformation/planarization of the amorphous chains and aggregates.

In the high concentration regime (0.05 mg/mL), shown in Fig. 5(c), the difference between the $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (270 μL) (olive solid curve) and $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (450 μL) (wine solid curve) are rather small. Therefore, the main conclusions addressed in Section 3.1 hold here. At this concentration, the A_1/A_2 ratios are 0.99, 0.77, and 0.72 for the solutions with 90, 270, and 450 μL of MeOH added, respectively (see Table 1). The vibronic progression A_3 is strong in the solutions where 270 and 450 μL are added, and once more both A_3/A_2 ratios are the same: 0.92, which is in agreement with an enhancement in the H-aggregates' J_{inter} . As summarized in Table 1, $W(J_{\text{inter}}) = 0.5$ meV (0.14 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (90 μL), $W(J_{\text{inter}}) = 71$ meV (18 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (270 μL), and $W(J_{\text{inter}}) = 90$ meV (22 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{MeOH}$ (450 μL). The increase of MeOH aliquots combined with the increase in concentration is enhancing the H-type character of the aggregates formed, such a combination seems to offer more room for controlling the aggregates' properties, including conjugation length (crystalline quality) of the species in a solution.

Fig. 5(b) shows representative Abs spectra for solutions (concentration 0.005 mg/mL) of $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ at 0 hrs (black solid curve), $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ at 24 hrs (gray solid curve), $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (90 μL) (navy solid curve), $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (270 μL) (olive solid curve), and $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (450 μL) (wine solid curve). As summarized in Table 1, the A_1/A_2 ratios are 0.85 (for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$), 0.93 (for both $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (90 μL) and $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (270 μL)), and 0.99 ($\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (450 μL)). Also in Table 1 is: $W(J_{\text{inter}}) = 44$ meV (11 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$, $W(J_{\text{inter}}) = 21$ meV (5 meV) for both $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (90 μL) and $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (270 μL), and $W(J_{\text{inter}}) = 2$ meV (0.57 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (450 μL). The values assumed by the parameters are in agreement with our previous discussions and C_5H_{10} seems to be an important player here. In fact, the effect of MeOH in stabilized CHCl_3 is essentially opposite to the effect observed for pure CHCl_3 : with increasing the amount of MeOH, $W(J_{\text{inter}})$ is decreasing, which suggests that the conjugation length and crystalline quality are increasing for these solutions. The H-aggregates are more weakly interacting, which is further confirmed by the decreasing A_3/A_2 ratios with increasing the MeOH aliquots (see Table 1).

In the high concentration regime (0.05 mg/mL), the A_1/A_2 ratios are 0.96 for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ and $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (90 μL), 0.91 for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (270 μL), and 0.85 ($\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (450 μL)). In addition (see Table 1): $W(J_{\text{inter}}) = 10$ meV (2 meV) for both $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ and $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (90 μL), $W(J_{\text{inter}}) = 26$ meV (7 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (270 μL), and $W(J_{\text{inter}}) = 45$ meV (11 meV) for $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (450 μL). This time around, the increase of MeOH aliquots combined with the increase in concentration is once again enhancing the H-type character of the aggregates formed (the A_3/A_2 ratios endorse this conclusion, see Table 1). The gradual increase in W suggests that the conjugation length and the aggregates' crystalline quality are decreasing for these solutions. The results here are similar to the high concentration solutions of pure CHCl_3 but much less

pronounced (i.e. J_{inter} and W about 50 % smaller), which is an additional confirmation that C_5H_{10} is in fact rendering MeOH less effective. Differently from the low concentration case, the Abs crossing point between the $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10}$ and $\text{P3HT}/\text{CHCl}_3 + \text{C}_5\text{H}_{10} + \text{MeOH}$ (450 μL) is much closer to the crossing points observed for the other solutions. This suggests that an isosbestic point is being recovered and so it is the one to one conversion from amorphous chains into ordered aggregates.

4. Conclusions

In this manuscript, H-aggregate formation in CHCl_3 -based P3HT solutions is used as probes to investigate the role of C_5H_{10} and its association with MeOH in determining the solvent's quality. It is shown that pure and C_5H_{10} -stabilized CHCl_3 lead to distinct aggregate properties in both their pristine and MeOH-modified conditions. It is seen that C_5H_{10} renders MeOH ineffective to alter the CHCl_3 polarity, to control the amount of aggregate formation as well as to control the planarity and crystallinity of the aggregates formed. In addition, it is seen that C_5H_{10} , which is often used as a CHCl_3 stabilizer, limits the lifespan of CHCl_3 as a good solvent, leading to aggregate formation in 24 h after solution preparation. Moreover, it is shown that the combination of both C_5H_{10} and several aliquots of MeOH opens up additional routes for controlling both the exciton bandwidth and J_{inter} magnitude when compared with routes where only aliquots of MeOH are changed.

CRediT authorship contribution statement

Huan Nguyen: Conceptualization, Data curation, Formal analysis, Investigation, Validation, Writing – original draft, Software. **Ruan L.S. Lima:** Conceptualization, Data curation, Formal analysis, Investigation, Validation, Writing – original draft, Software. **Newton M. Barbosa Neto:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Paulo T. Araujo:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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