Supporting Information

Ultrafast homogeneous glycolysis of waste polyethylene terephthalate via a dissolution-degradation strategy

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S1 Product characterizations of PET glycolysis in homogenous system

The key point of dissolution-degradation strategy for PET recycling is to search out a solvent which has good solubility to PET and does not react with PET and EG. Therefore, whether the product is BHET is an important criterion for testing whether the solvent can be used in PET glycolysis. Four solvents, including aniline, nitrobenzene, NMP and DMSO, were screened out from a series of solvents to be used in this strategy. In order to prove that the products obtained in these four solvents are all BHET, several kinds of characterizations were carried out, such as HPLC, NMR, ESI-MS, FT-IR, elemental analysis and ICP. Figure S1 shows the ^{1}H NMR of main products, it can be seen that the signal of product in different solvents is the same, which represents that the product in different solvents should be the same substance. The signal at δ 8.13 ppm represents the aromatic protons in benzene ring. The signals at δ 4.34 ppm and 3.75 ppm indicate the methylene protons in COO-CH_2 and CH_2-OH, respectively. The signal at δ 4.98 ppm represents the proton in hydroxyl. Hence, the main product is identified to be BHET. Figure S2 depicts that the highest peaks are m/e 277 in different solvents, which are related to the main product ionized by Na^+. Therefore, the real molecular weight of the main product is 254 g/mol, which is the same with BHET.

The HPLC graph of main product in different solvents (Figure S3) shows that the appearance time are 29.5 min, which is identified as BHET. And the product is highly pure because there is no other peak except the solvent peak at 25.8 min. It can be clearly seen that the spectrograph of four solvents result are the same, which contain a -OH band at 3447 cm^{-1} and 1134 cm^{-1}, a C=O stretching at 1715 cm^{-1}, an alkyl C-H at 2880 cm^{-1} and 2963 cm^{-1}, and an aromatic C-H at 1457cm^{-1} from the Figure S4. The element analysis results (Table S1) illustrate that all products obtained in four solvents, the content of C, H and O are very similar with BHET obtained in EG and theoretical value, respectively. The products obtained in different solvents are all white needle-like crystals, which are the same with BHET obtained in EG. Furthermore, it is shown that aniline has not reacted with PET in present of EG, according to the results

of GC-MS (Figure S6). The European Union Food Plastics Regulations (No.10/2011) stipulates that the content of zinc in PET cannot exceed 5 mg/kg. The ICP results (Table S2) depict that the content of zinc ion in product obtained in four solvents are lower than 5 mg/kg, which is satisfied with requirement of re-polymerization. In consequence, the products of PET glycolysis in four different solvents are all BHET, and the purity of BHET is satisfied with the demand of repolymerization.

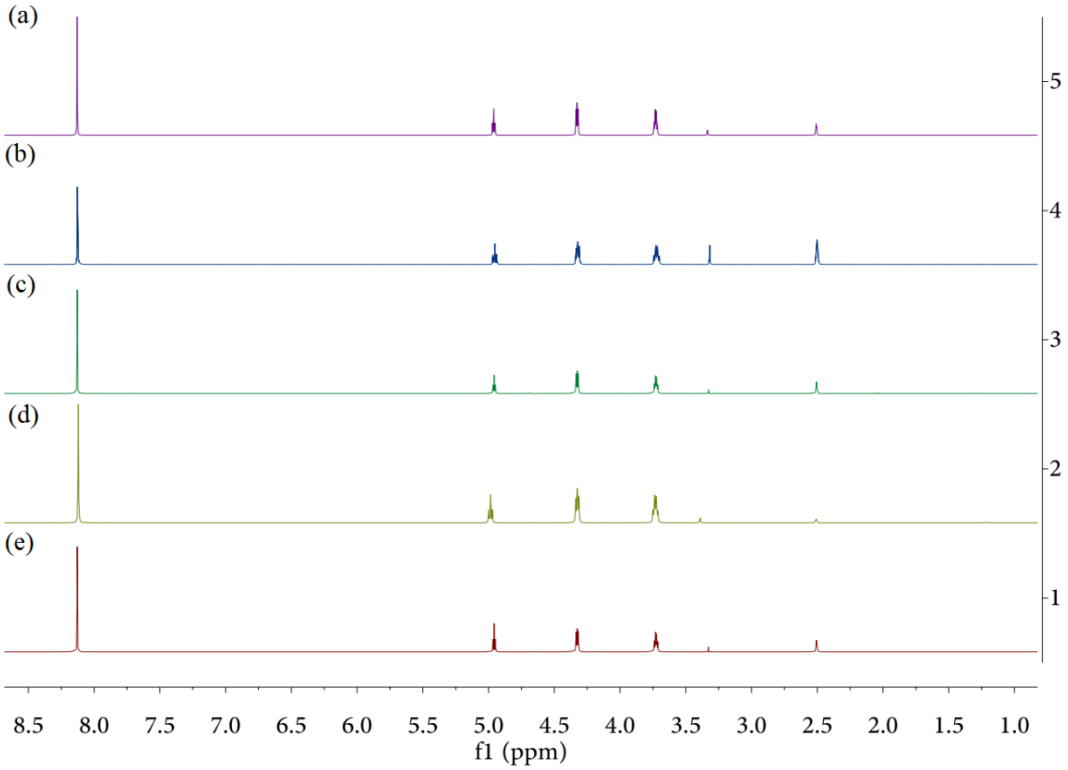

Fig. S1 ^{1}H NMR spectra of the main product of PET glycolysis in different solvents, respectively (a) DMSO (b) NMP (c) Aniline (d) Nitrobenzene (e) EG.

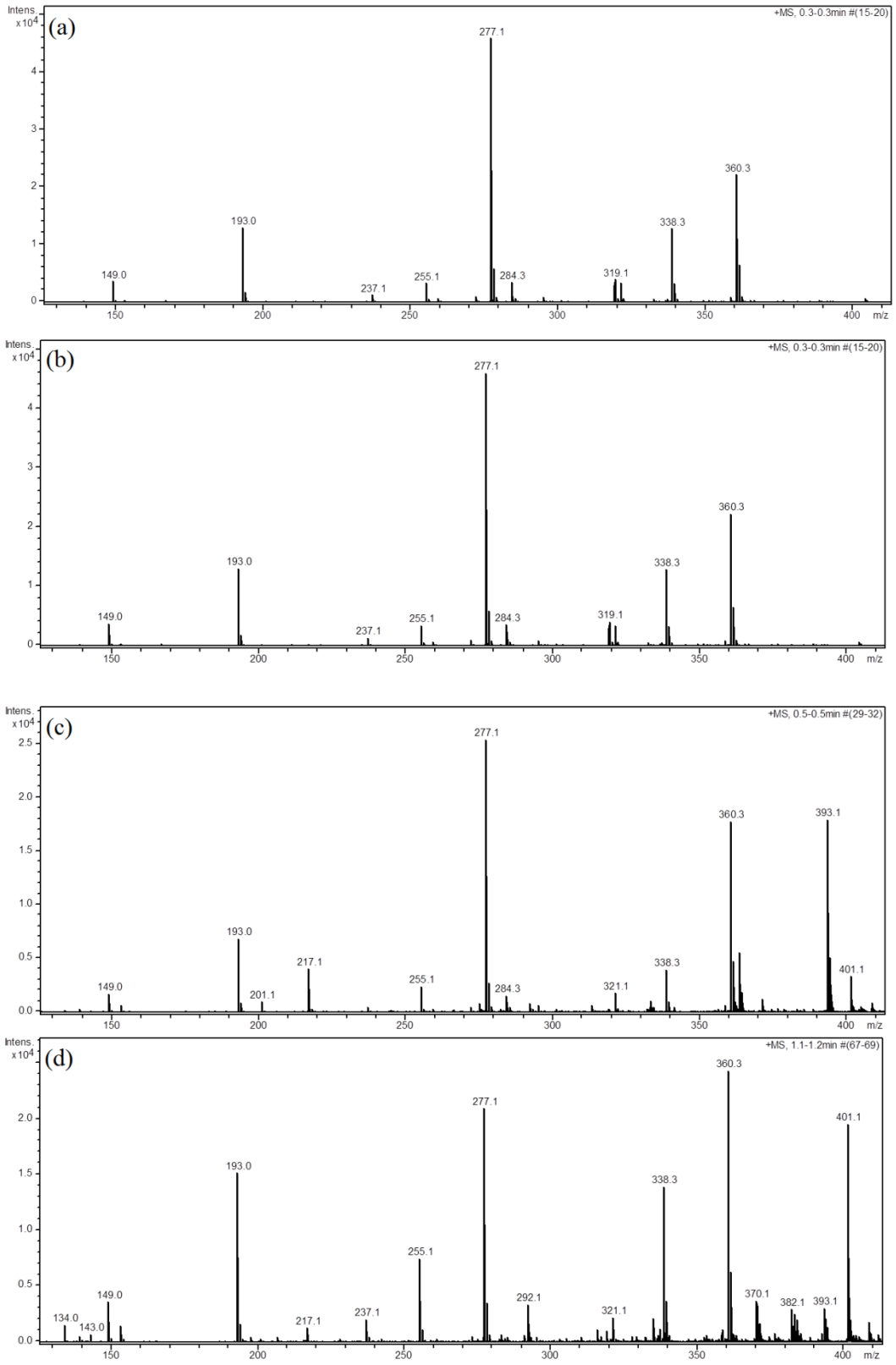

Fig. S2 ESI-MS spectra of the main product of PET glycolysis in different solvents, respectively

(a) DMSO (b) NMP (c) Aniline (d) Nitrobenzene.

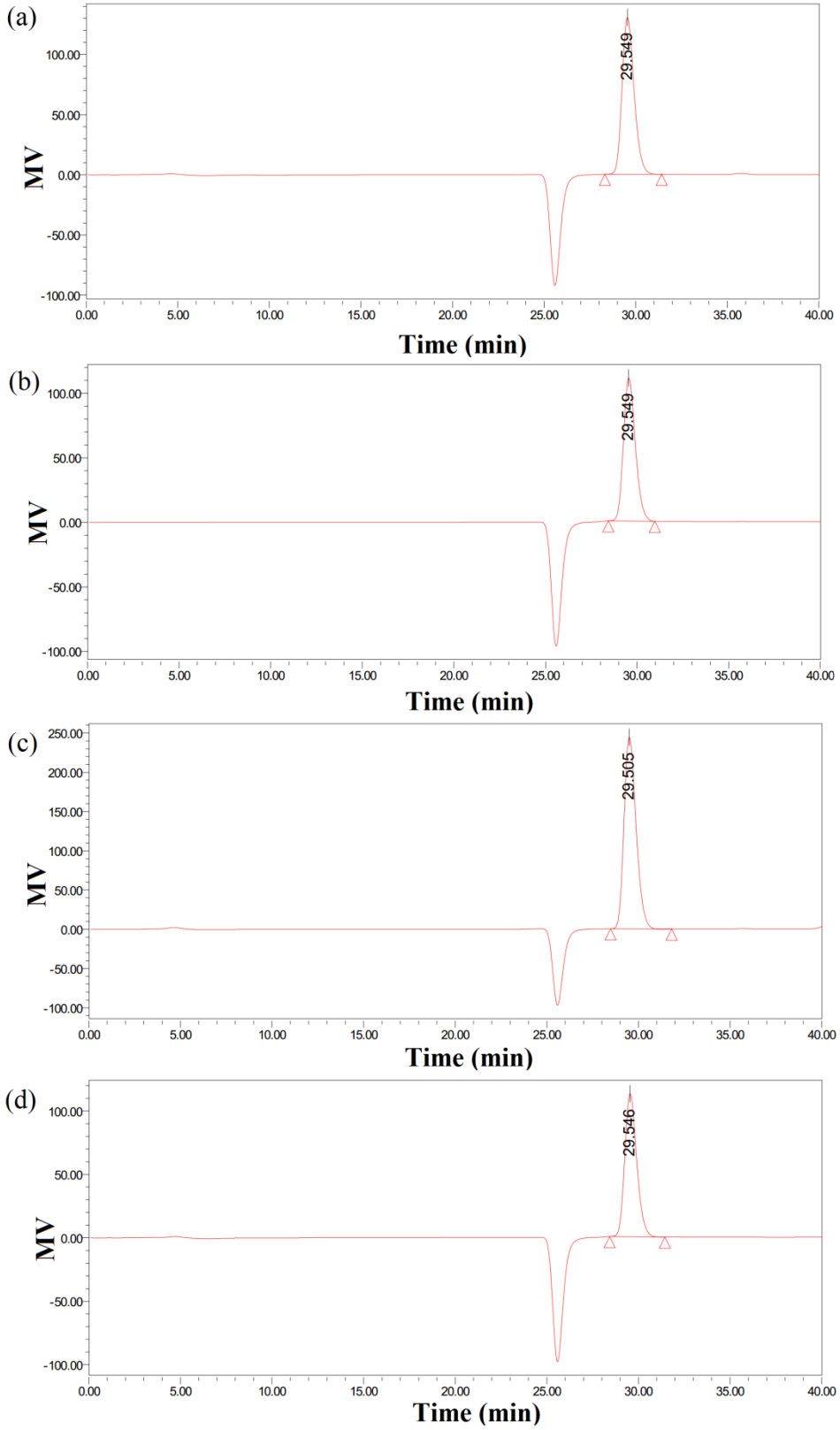

Fig. S3 HPLC results of the main product of PET glycolysis in different solvents, respectively (a) DMSO (b) NMP (c) aniline (d) nitrobenzene.

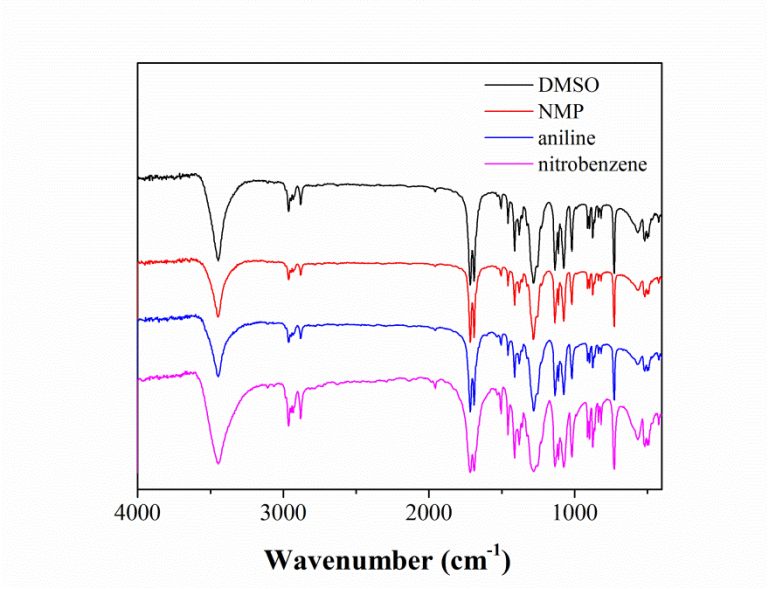

Fig. S4 FT-IR spectrum of the main product of PET glycolysis in different solvents, respectively

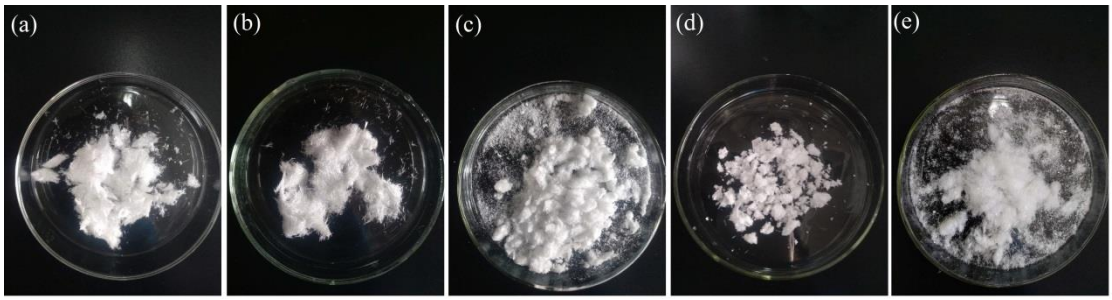

Fig. S5 Products of PET glycolysis in different solvents, respectively. (a) DMSO, (b) NMP, (c) aniline, (d) nitrobenzene, (e) EG

Table S1 Element analysis results of the main product of PET glycolysis in different solvents, respectively

Element	C/%	H/%	O/%	N/%
NMP	56.94	5.68	37.37	0
DMSO	56.87	5.64	37.49	0
$PhNH_2$	57.81	5.67	36.42	0.1
$PhNO_2$	56.86	5.62	37.51	0
EG	56.62	5.65	37.74	0
theoretical value	56.70	5.54	37.76	0

Table S2 ICP results of the main product of PET glycolysis in different solvents, respectively

Solvents	Weight of sample/mg	C_{Zn}/mg·L^{-3}	Content of Zn/10^{-6}
NMP	22.4	0.022	4.9
DMSO	30.8	0.020	3.2
$PhNH_2$	25.8	0.025	4.8
$PhNO_2$	27.0	0.026	4.8

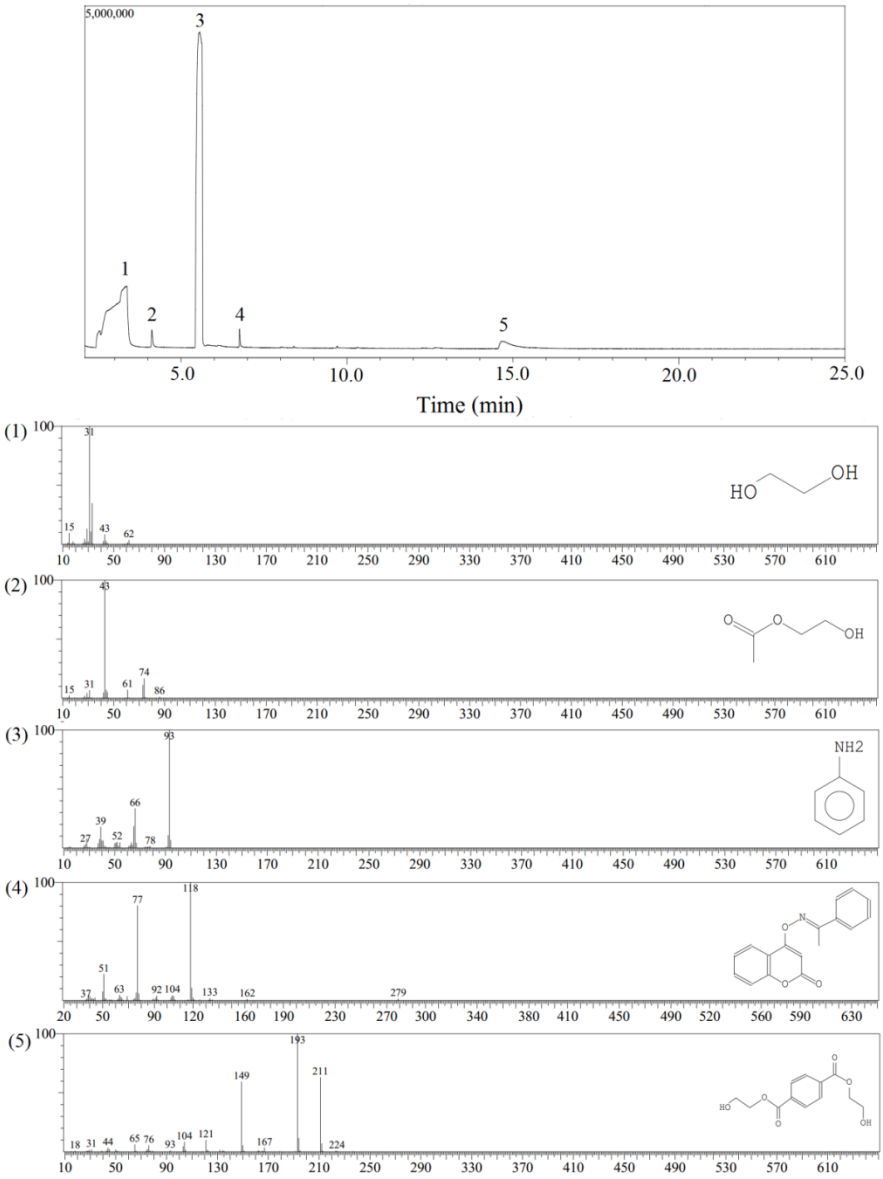

Fig. S6 GC-MS result of reaction solution using aniline as solvent.

S2 Solubility and solubility heat of PET in different solvents

The solubility of PET in different solvents was investigated. The results of figure S7 showed that the saturation concentration order of PET in different solvents is aniline > NMP > nitrobenzene > DMSO at the same temperature condition. Furthermore, the solubility of PET in these four solvents increased with the raising of temperature, which indicated that the dissolution of PET should be an endothermic process. To understand the solubility order, the dissolution heat of PET in these four solvents was measured via reaction calorimeter. Table S3 shows the result of dissolution heat of PET in different solvents. It can be seen that the dissolution heats are negative which means they are all endothermic. And the order of heat absorption capacity is aniline < NMP < nitrobenzene < DMSO, which is completely reverse to the order of saturation concentration of PET. That is because the value of dissolution heat is higher; the interaction between PET and solvent is weaker. The phenomenon presented at macro level is that PET is hard to dissolve in solvent.

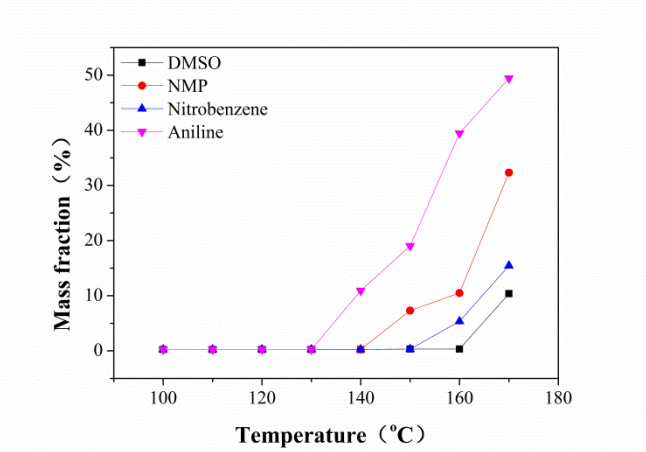

Fig.S7 The changes of solubility of PET with temperature in different solvents.

Table S3 Dissolution heat of PET in different solvents

Solvents	Dissolution heat/kJ·mol^{-1}
$PhNH_2$	-12.46
NMP	-15.03
$PhNO_2$	-17.71
DMSO	-19.46

S3 DFT calculation

All the DFT calculations are carried out with Gaussian 09 package. Geometries of PET and solvent molecules are fully optimized at M062X-D3/6-31+G** level which could be used in the studies of noncovalent interactions. To account for the effects of solution environment around the molecules, calculations are performed in different solvent using the polarizable continuum model (PCM) developed by Tomasi and co-workers. Vibrational frequencies are calculated to verify the stationary structure for all the configures. The binding energies for PET and different solvents are defined as follows:

$$\Delta E(\mathrm{kcal/mol}) = 627.51 * [E_{AB(au)} - (E_{A(au)} - E_{B(au)})]$$

To further study noncovalent interaction reduced density gradient (RDG) analysis is employed in this work. The regions and types of interactions between PET and solvent molecule can also be visualized by colored RDG isosurface. The blue region denotes van der Waals interaction and weak H-bond interaction, the green region indicates van der Waals interaction and steric effect coexist at the same time, while the red region shows the steric effect. Hence, we can make the conclusion that there is big π-stacking in the Dimer-PHAN.

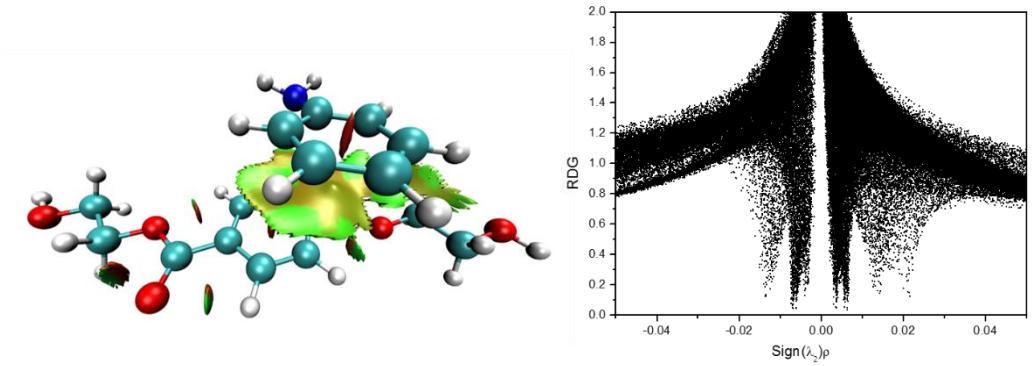

Fig. S8 RDG isosurfaces (s=0.6 a.u.) and surface plots of PET-PHAN interaction. The isosurfaces are colored on a blue-green-red scale according to values of sign(λ2)ρ, ranging from -0.05 to 0.05 a.u. Red indicates strong attractive interactions, and blue indicates strong nonbonded overlap

S4 Solubility of PET in naphthalene and tetrahydronaphthalene

We measured the solubility of PET in these two solvents at 185 degree centigrade. The results depicted that PET had well solubility in naphthalene (4.8g PET dissolved in 20 g naphthalene) but poor solubility in tetrahydronaphthalene (less than 0.1g PET dissolved in 20 g tetrahydronaphthalene). Considering that the aromaticity of naphthalene is better than tetrahydronaphthalene, this result should prove our assumption from the side.