

Supplementary Materials for

Novel photo-responsive deep eutectic solvents: preparation, characterization, and application in detecting trace organophosphorus pesticide residues in apples and grapes

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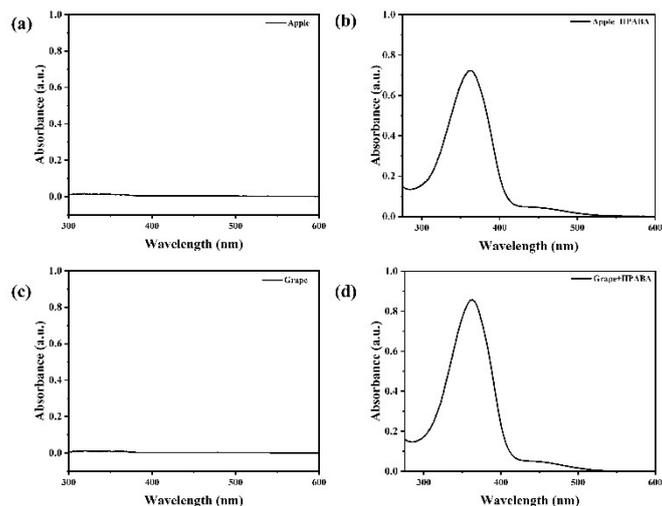


Fig. S1. Ultraviolet-visible absorption spectra of blank fruit extract and blank fruit extract in the presence of $35 \mu\text{mol L}^{-1}$ HPABA in THF (a: Apple, b: Apple+HPABA, c: Grape, d: Grape+HPABA)

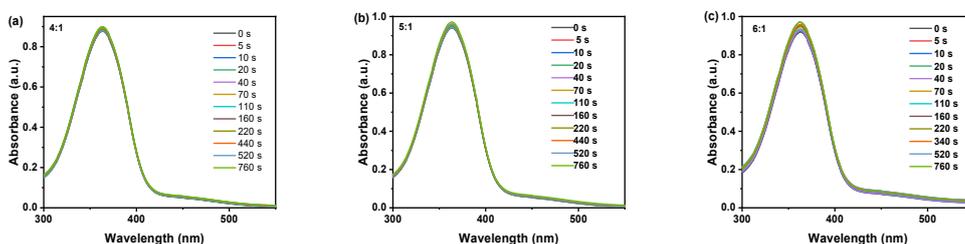


Fig. S2. UV-Vis spectral changes of the DESs formed from TBAB and HPABA with a molar ratio of 4:1 (a), 5:1 (b) and 6:1 (c) in THF (HPABA concentration: $35 \mu\text{mol L}^{-1}$) upon irradiation at 365 nm for different times.

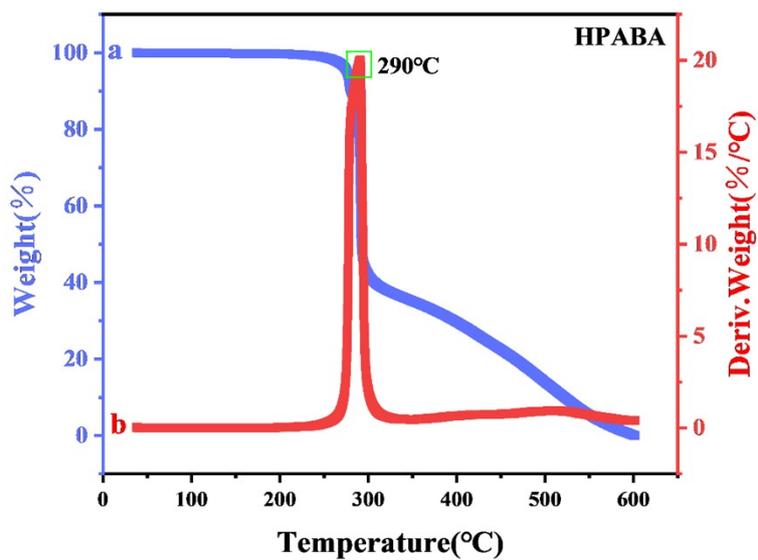


Fig. S3. Thermogravimetric analysis and derivative thermogravimetry of HPABA.

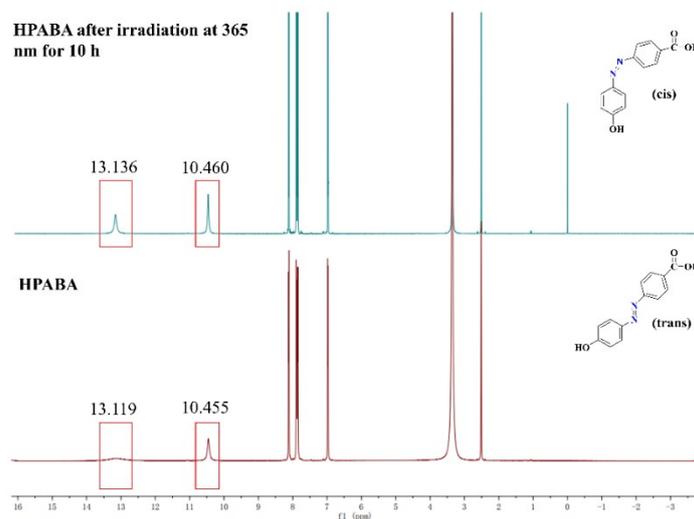


Fig. S4. ^1H NMR spectra of HPABA upon irradiation for 10 h at 365 nm in $\text{DMSO}-d_6$

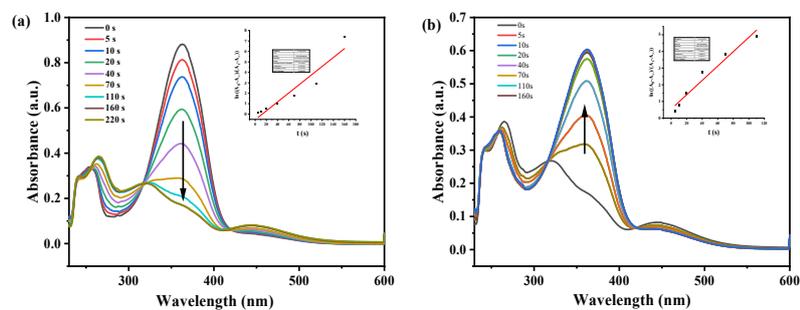


Fig. S5. UV-Vis absorption spectra of HPABA in THF ($35 \mu\text{mol L}^{-1}$) upon irradiation at 365 nm (a) and 440 nm (b) for different times.

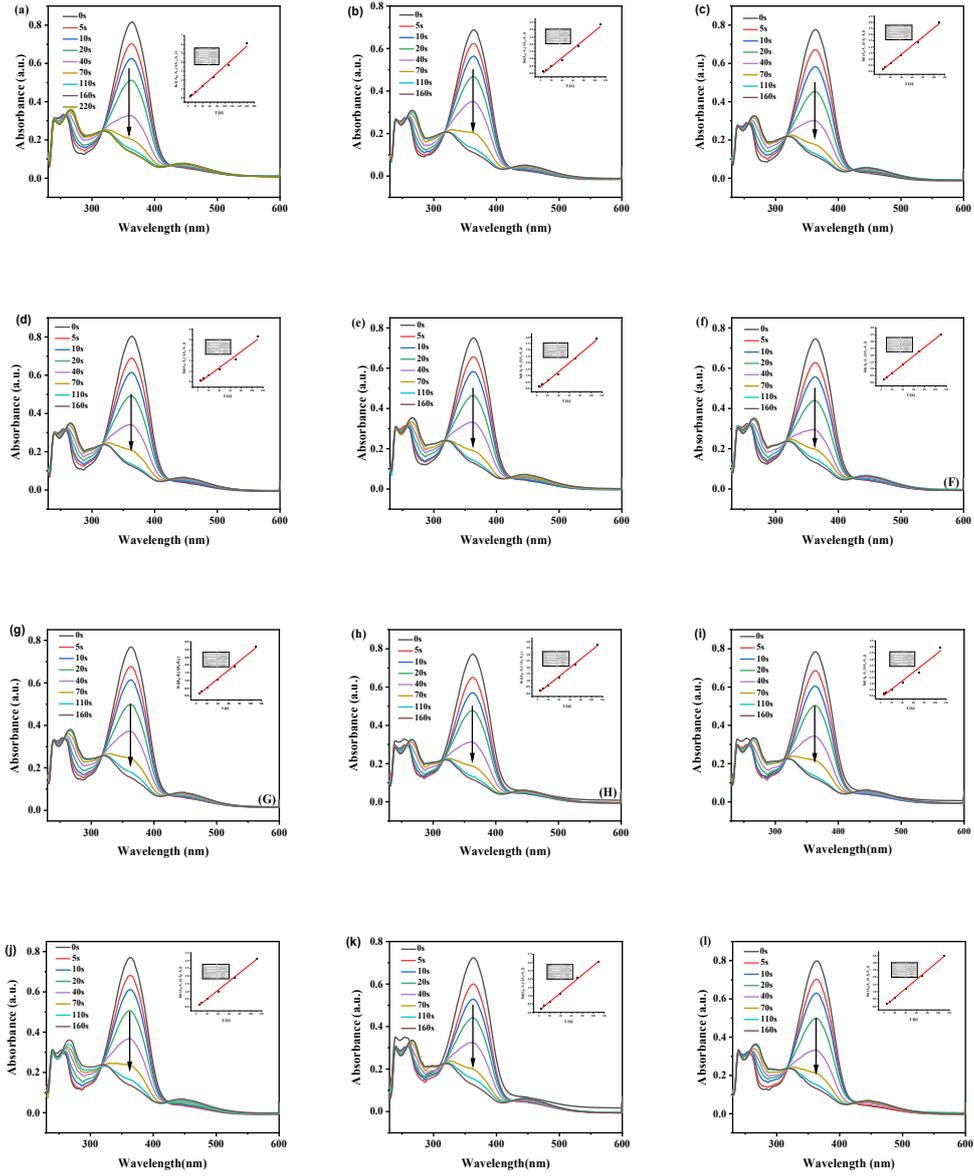


Fig. S6. UV-Vis absorption spectra of CPF-PR-DESs at different CPF concentrations: (a) 0.0 $\mu\text{g/L}$, (b) 50 $\mu\text{g/L}$, (c) 100 $\mu\text{g/L}$, (d) 200 $\mu\text{g/L}$, (e) 300 $\mu\text{g/L}$, (f) 400 $\mu\text{g/L}$, (g) 500 $\mu\text{g/L}$, (h) 600 $\mu\text{g/L}$, (i) 700 $\mu\text{g/L}$, (j) 800 $\mu\text{g/L}$, (l) 900 $\mu\text{g/L}$, (l) 1000 $\mu\text{g/L}$.

Table S1 The *trans*→*cis* photoisomerization rate constant ($k_{trans\rightarrow cis}$) of HPABA within the PR-DES at different CPF concentrations

CPF concentration ($\mu\text{g/L}$)	$k_{trans\rightarrow cis}$ (s^{-1})			Averaged value
	k_1	k_2	k_3	
0	0.01974	0.03496	0.03743	0.03071
50	0.03047	0.0308	0.0319	0.0319
100	0.03512	0.03599	0.03226	0.03226
200	0.03797	0.03	0.032	0.0333
300	0.035	0.0366	0.0315	0.0343
400	0.03155	0.03853	0.0345	0.0348
500	0.02847	0.03849	0.041	0.0357
600	0.03363	0.03578	0.03878	0.0364
700	0.03481	0.0401	0.0376	0.0374
800	0.03811	0.04	0.03792	0.03867
900	0.0382	0.0421	0.0361	0.0391
1000	0.04036	0.04239	0.03833	0.04036

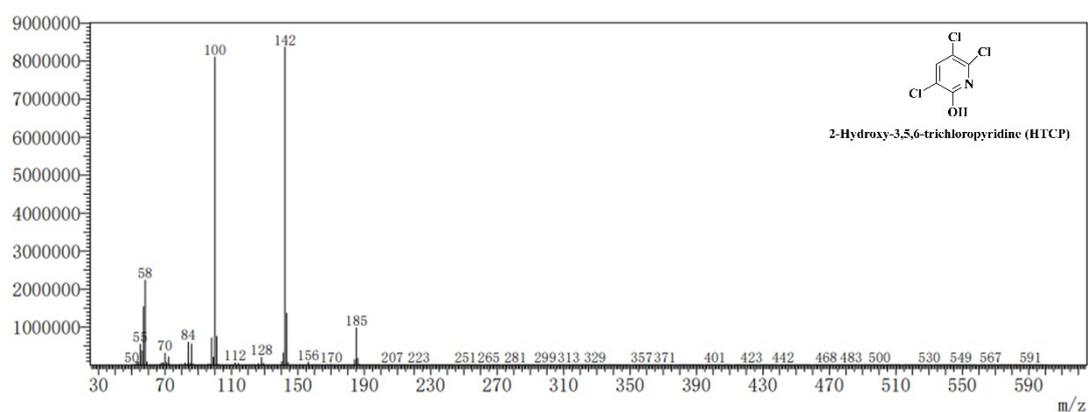


Fig. S7. Mass spectrum of 2-hydroxy-3,5,6-trichloropyridine

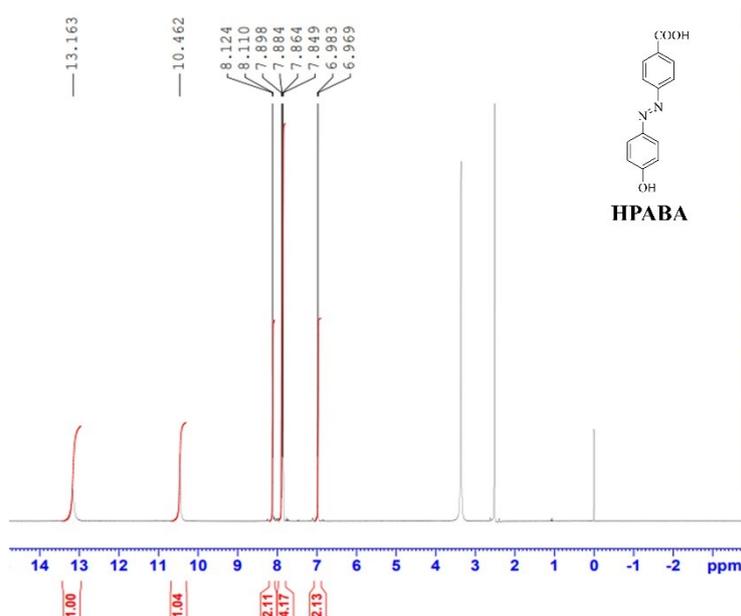


Fig. S8. ^1H NMR spectrum of HPABA recovered via acid precipitation from the filtrate.

Table S2 Extraction and detection of CPM and ACV in fruits by PR-DES methods

Fruits	Analyte	Added ($\mu\text{g}\cdot\text{g}^{-1}$)	Extraction Efficiency (%)	Found ($\mu\text{g}\cdot\text{g}^{-1}$)	Recovery (%)	RSD(n=3) (%)
Apple	CPM	0.500	99.62%	0.493	98.6	3.47
	ACV	0.500	99.16%	-	-	-
	CPM+CPF	0.500+0.500	99.01%	0.983	98.3	4.16
	ACV+CPF	0.500+0.500	98.93%	0.425	42.5	3.78
	CPM+ACV	0.500+0.500	98.78%	0.437	43.7	2.12
Grape	CPM	0.500	99.57%	0.488	97.6	1.09
	ACV	0.500	99.10%	-	-	-
	CPM+CPF	0.500+0.500	99.69%	0.976	97.6	2.86
	ACV+CPF	0.500+0.500	99.26%	0.446	44.6	1.58
	CPM+ACV	0.500+0.500	99.19%	0.458	45.8	2.69

Table S3 CPF residue determination in fruits and recovery in samples with the non-photoresponsive DES

Fruits	Added ($\mu\text{g}\cdot\text{g}^{-1}$)	Found ($\mu\text{g}\cdot\text{g}^{-1}$)	Recovery (%)	RSD (n=3) (%)
Apple	0.000	0.000	-	-
	0.500	0.423	84.60%	4.19
	1.000	0.856	85.60%	3.88
Grape	0.000	0.000	-	-
	0.500	0.456	91.20%	3.63
	1.000	0.874	87.40%	3.87

Table S4 Comparison of the PR-DES based method with other analytical methods for CPF detection in environmental and food samples

Matrix	Pretreatment Method	Adsorbent Solvent	Recovery (%)	Limit of Detection	of Detection Method	Ref.
Rice	MSPE ^a	MFCs ^b /Ethanol MFCs ^b /	88.0-91.8	1.0 $\mu\text{g L}^{-1}$	HPLC-UV	34
Wheat	SSPME ^c	Acetonitrile- acetate buffer	97.9	20.0 $\mu\text{g kg}^{-1}$	GC-FID ^d	35
Cereals	DLLME ^e	DES-FA ^f	86.7-99.9	0.0006 $\mu\text{g kg}^{-1}$	ELISA- UV	36
Water	Thin film microextraction	DES	64-72	0.7 $\mu\text{g L}^{-1}$	GC-MS	37
Vegetables	VA-MDES- SEEME ^g	DES	92.8-97.5	0.09 $\mu\text{g L}^{-1}$	UV-Vis	38
Fruits	LA-SPE ^h	PR-DES	98.6-100.4	16.19 $\mu\text{g L}^{-1}$	UV-Vis	This work

^a MSPE: Magnetic solid-phase extraction

^b MFC: Magnetic frameworks composites

^c SSPME: Smart solid-phase microextraction

^d GC-FID: Gas chromatography-flame ionization detector

^e DLLME: Dispersive liquid-liquid microextraction

^f FA: Fatty acids

^g VA-MDES-SEEME: Vortex-assisted magnetic deep eutectic solvent-based surfactant-enhanced emulsification microextraction

^h LA-SPE: Light-assisted solid-phase extraction