Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Light-driven Fluorescence Enhancement and Self-assembled Structural Evolution of an Azobenzene Derivative

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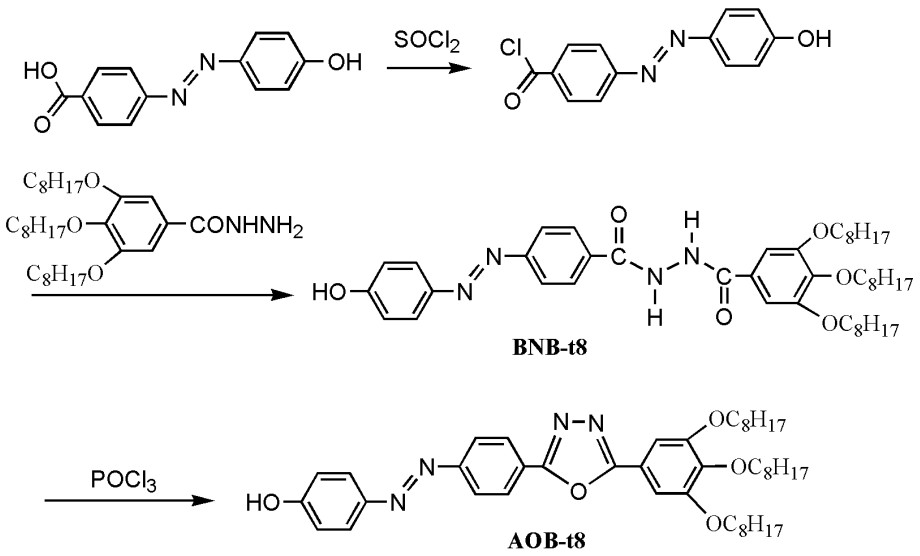
Synthesis

Scheme S1. Synthetic route for AOB-t8



The compound, N-(3,4,5-octanoxyphenyl)-N'-4-[(4-hydroxyphenyl) azophenyl] 1,3,4-oxadiazole (AOB-t8), was synthesized following the mechanism shown in Scheme S1. The hydrazine derivatives BNB-t8 were prepared by the route reported in our previous work [12]. The purified BNB-t8 was dissolved in phosphorous oxychloride ($POCl_3$) and refluxed for about 40 h. The excess $POCl_3$ was removed through distillation and the residue was slowly added to ice-water. After removal of the solvent

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under a reduced pressure, the final product AOB-t8 was purified by recrystallization from ethanol for further NMR, FT-IR spectroscopy and elemental analysis.

N-(3,4,5-octanoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl] 1,3,4-oxadiazole (AOB-t8)

^{1}H NMR (400MHz, DMSO-d_6), (ppm, from TMS): 8.35 (d, 2H, J=8.4), 8.06 (d, 2H, J=8.8), 7.97 (d, 2H, J=8.8), 7.40 (d, 2H, J=9.2), 7.36 (s, 2H), 4.05-3.93 (m, 6H), 1.88-1.64 (m, 6H), 1.47-1.23 (m, 30H), 0.87-0.84 (m, 9H).

FT-IR (KBr, pellet, cm^{-1}): 3426, 2956, 2925, 2855, 1592, 1551, 1494, 1468, 1440, 1386, 1326, 1292, 1227, 1119, 1029, 1009, 980, 855, 839, 746, 727.

Elemental analysis: calculated for $C_{44}H_{62}N_4O_5$ (%): C, 72.69; H, 8.60; N, 7.71. Found: C, 72.57; H, 8.85; N, 7.63.

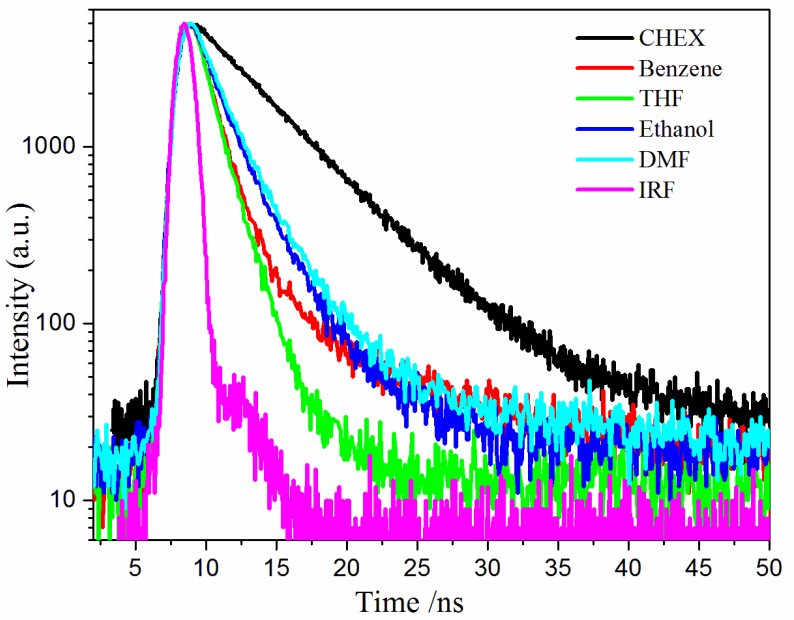


Fig. S1 Fluorescence lifetime decay profiles (excitation at 295 nm) of AOB-t8 in different solvents.

Table S1. Photophysical characteristics of AOB-t8 (1×10^{-5} M and 1×10^{-3} M) in ethanol at room temperature.

UV 365nm	1×10^{-5} mol/L			1×10^{-3} mol/L		
	λ_{abs} (nm)	λ_{em} (nm)	Φ_F ($\times10^{-2}$)	λ_{abs} (nm)	λ_{em} (nm)	Φ_F ($\times10^{-2}$)
0 min	365	434	**0.24**	357	436	**0.11**
30 min	-	-	0.62	356	435	0.13
50 min	297	386, 417,423	4.21	356	435	0.18
70 min	266	370, 416	**5.83**	-	-	-
130min	-	-	-	299, 354	424	0.26
240min	-	-	-	290	414	28.31
290min	-	-	-	270	380, 414	**33.71**

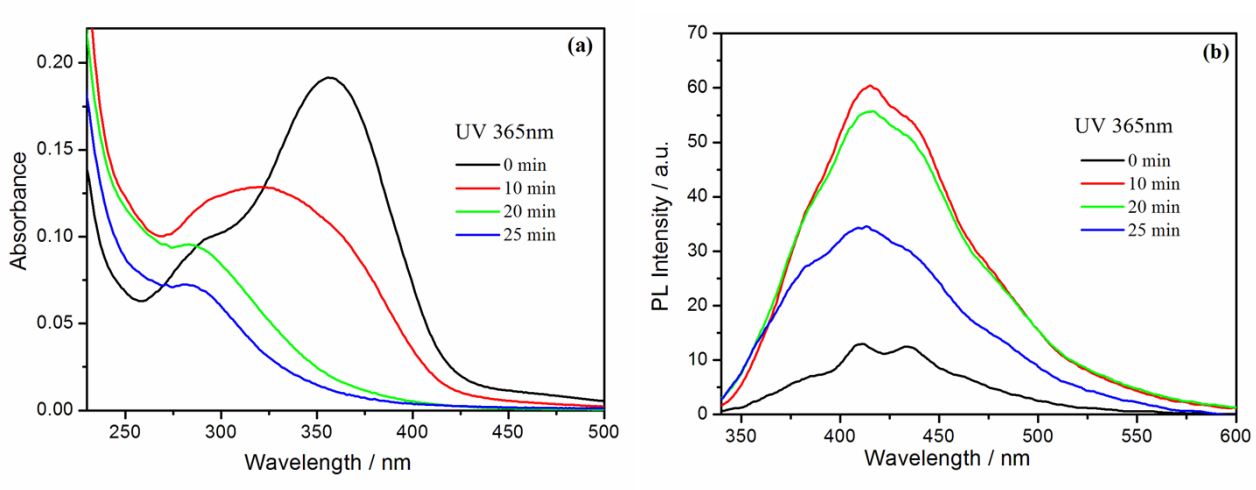


Fig. S2 (a) UV-vis and (b) fluorescence spectra of AOB-t8 in dichloromethane (1×10^{-5} M) under 365 nm irradiation for different time at room temperature.

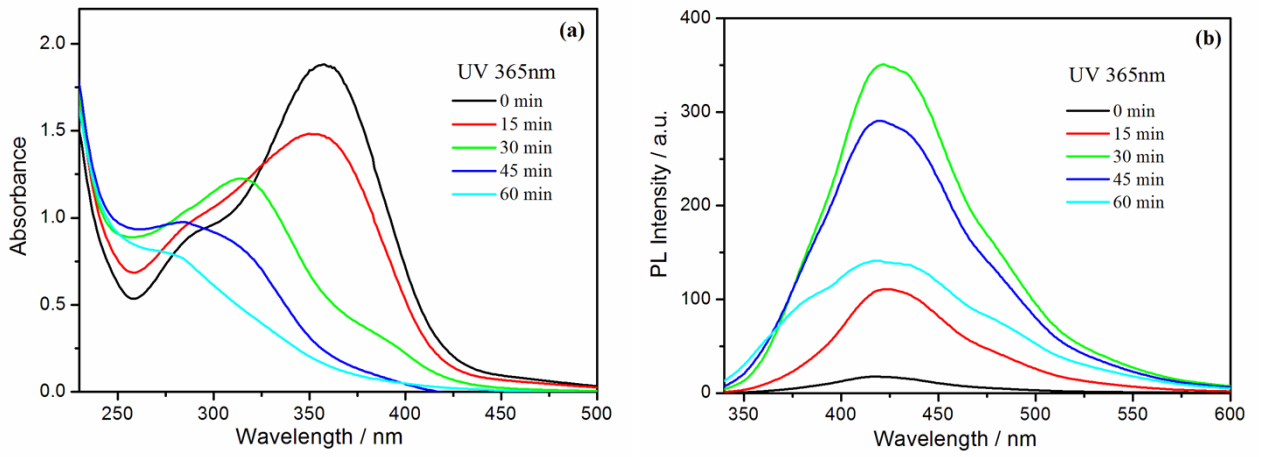
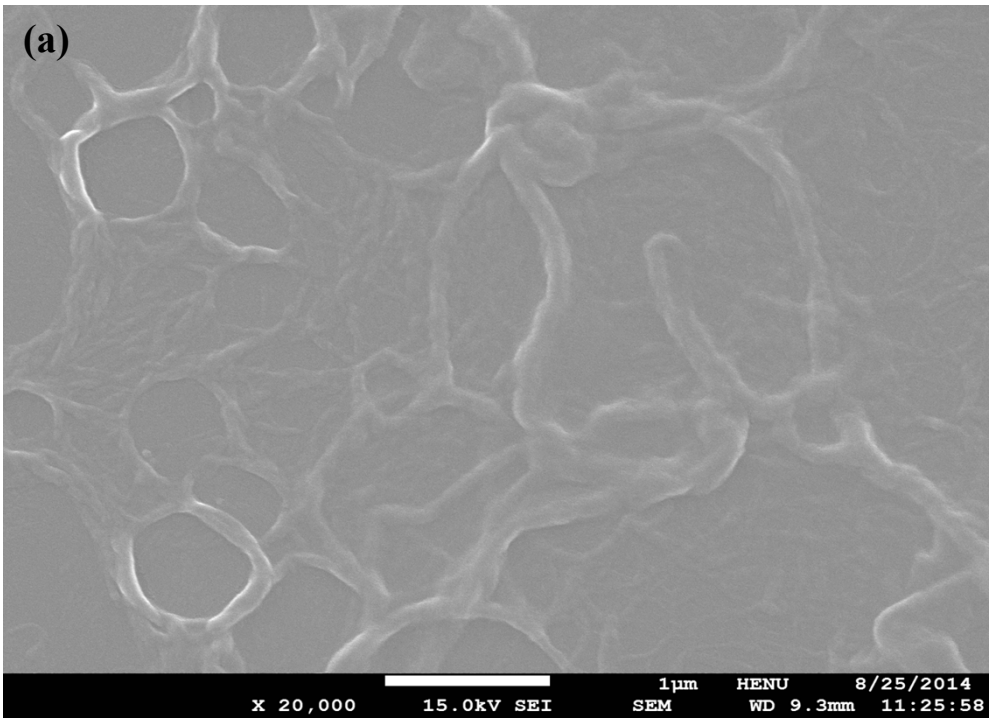
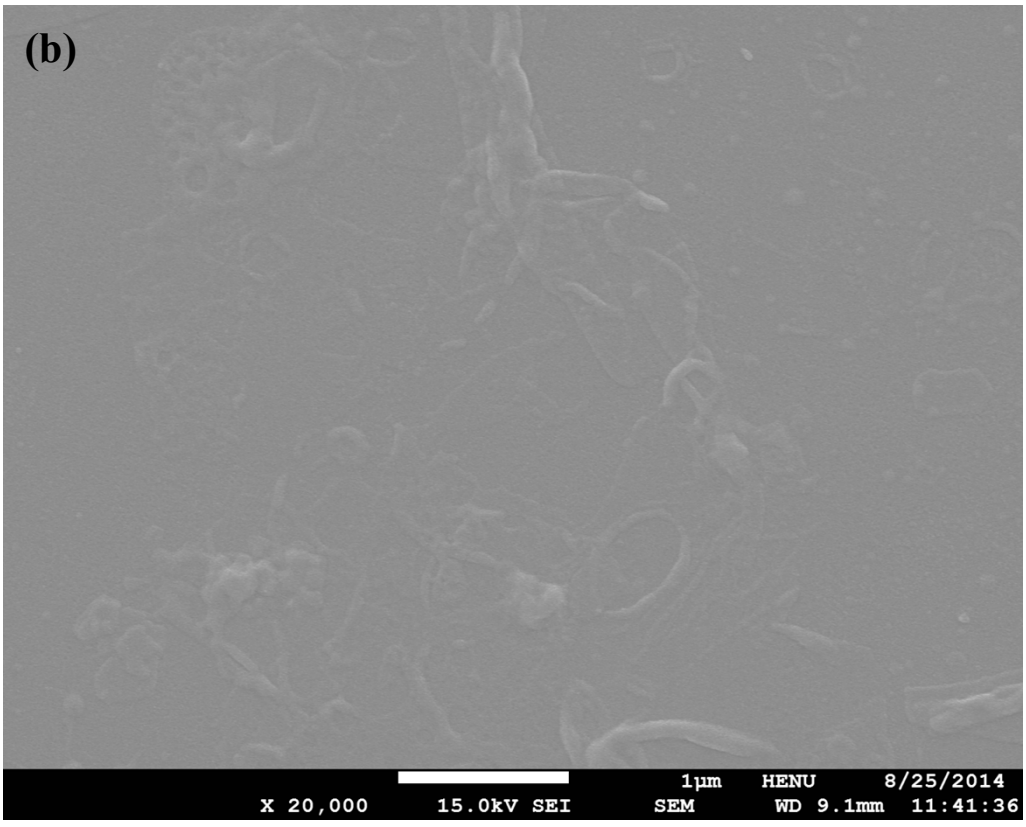


Fig. S3 (a) UV-vis and (b) fluorescence spectra of AOB-t8 in dichloromethane (1×10^{-3} M) under 365 nm irradiation for different time at room temperature.


(a)
X 20,000 15.0kV SEI
1μm HENU 8/25/2014
SEM WD 9.3mm 11:25:58


(b)
X 20,000 15.0kV SEI
1μm HENU 8/25/2014
SEM WD 9.1mm 11:41:36

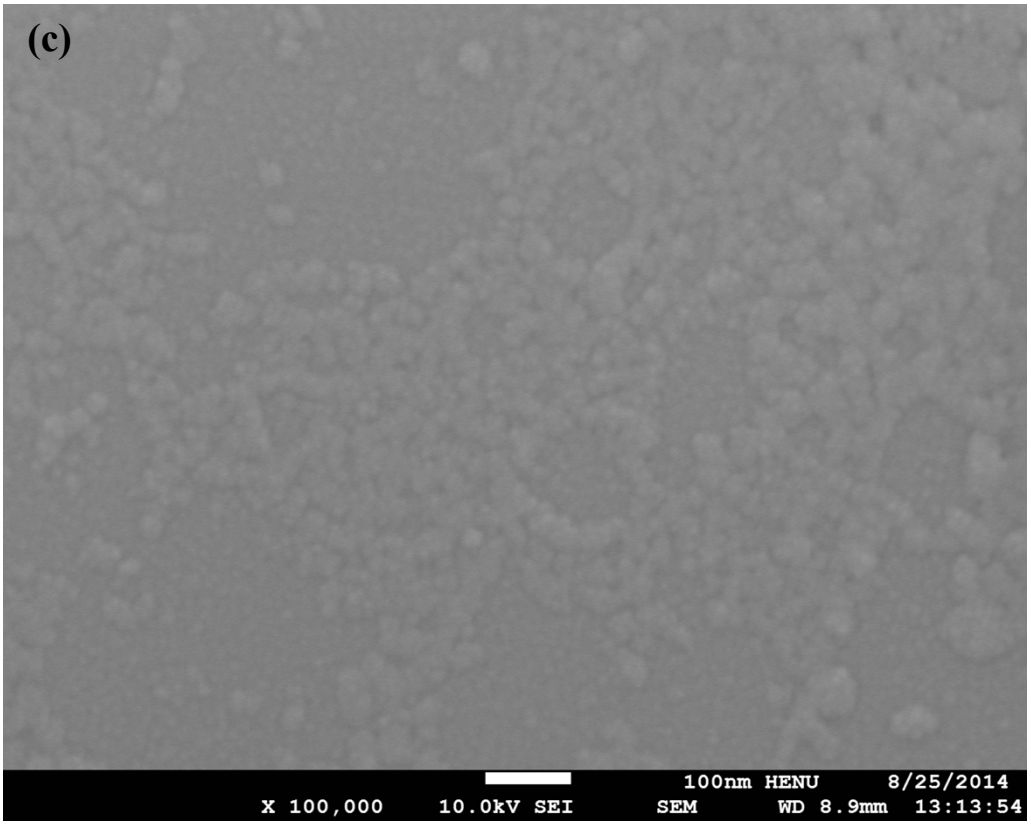
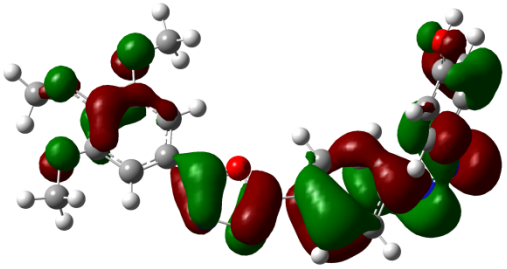
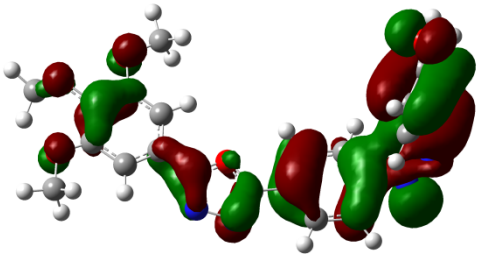


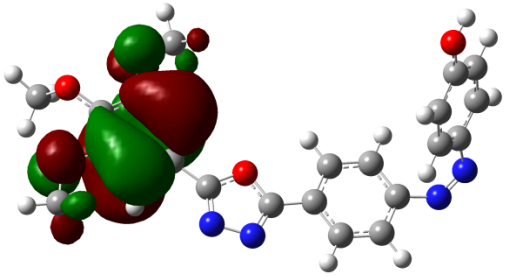
Fig. S4 SEM images of AOB-t8 in dichloromethane (1×10^{-5} M) (a) before UV light, (b) after exposure to UV light for 15 min and (c) for 25 min.



cis-109



cis -110



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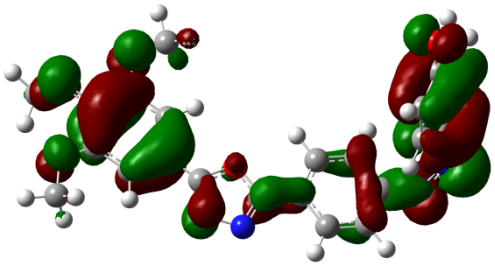
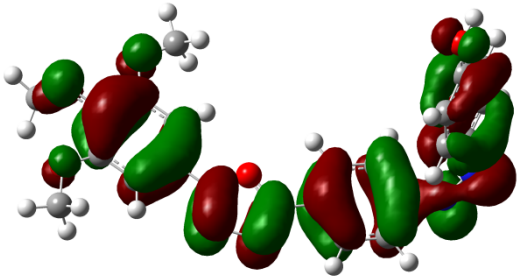
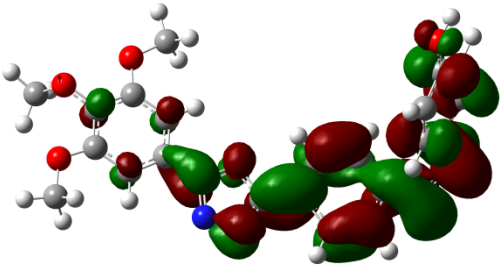


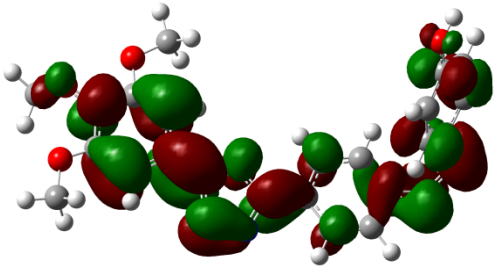
cis -112



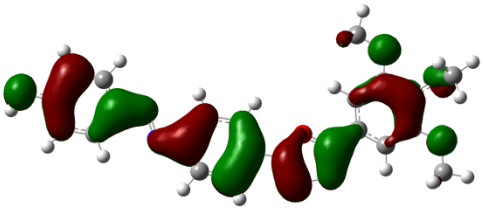
cis -113(HOMO)



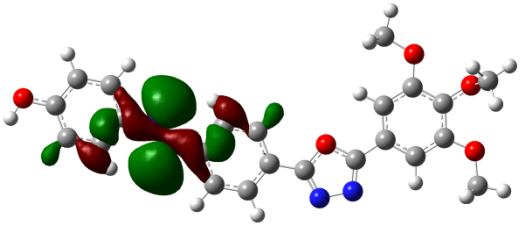
cis -114(LUMO)



cis -115



trans -109



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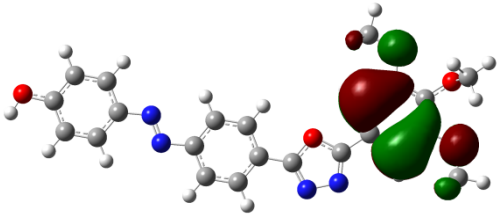

trans -111

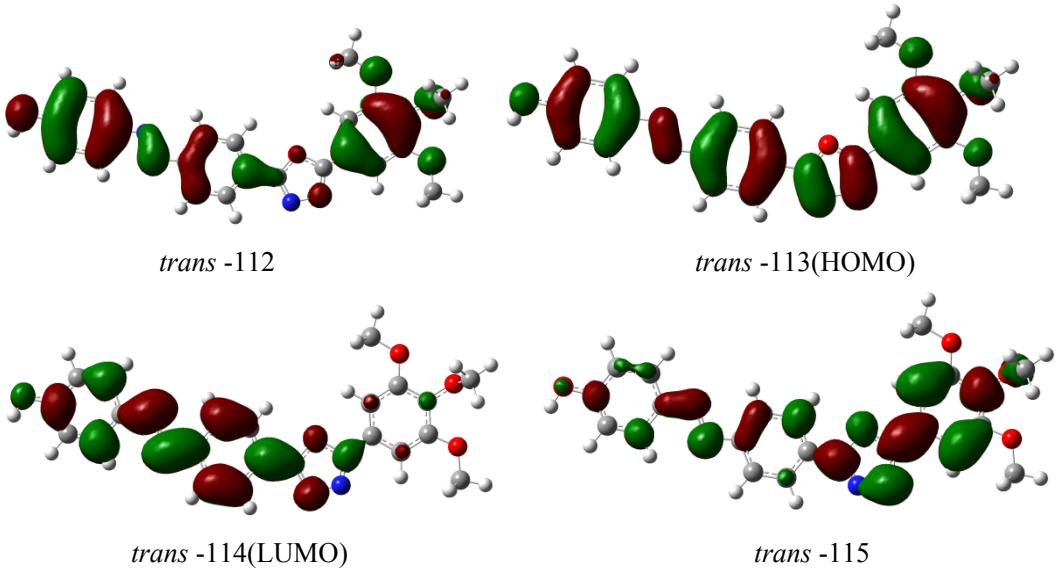

Fig. S5 Electron density diagrams of molecular orbitals of *trans*-AOB-t1 and *cis*-AOB-t1 computed with CAM-B3LYP/6-31G** method, respectively.