Electronic Supporting Information (ESI)

Aza-bicyclodiene based photoswitches for molecular solar thermal energy storage

Akanksha Ashok Sangolkar, Rama Krishna Kadiyam, and Ravinder Pawar*

Laboratory of Advanced Computation and Theory for Materials and Chemistry, Department of Chemistry, National Institute of Technology Warangal (NITW), Warangal, Telangana-506004, India.

ravinder_pawar@nitw.ac.in

S1: Ring strain energy (SE) and thermochemical properties of parent bridgehead modified bicyclodiene-based photoswitching systems.

Table S1. Ring strain energy (SE) and thermochemical properties of unsubstituted bridgehead modified bicyclodiene-based photoswitching systems.

Photoswitching system	Ring strain energy (kcal/mol)		Thermochemical properties (kJ/mol)	
	Bicyclodiene	Photoisomer	Storage energy	TBR
NBD/QC	28.95	89.75	96.06	121.76
BOD/TCO	11.16	95.08	186.19	75.45
BND/TCN	9.52	100.55	222.00	64.18
BDD/TCD	4.28	115.19	304.39	37.63

S2: Thermochemical properties

The storage energy and energy storage density are calculated by using the electronic energy computed at DLPNO-CCSD(T)/Def2TZVP and including the thermal correction of M062X/6-311++G** level. The transition state (TS) geometries are obtained *via* climbing image nudged elastic band (CI-NEB) calculations using GGA-PBE functional. The thermal back reaction barrier is estimated by computing the electronic energy of the TS and product with (8,8)-CASPT2/6-311++G** level of theory.

Table S2: The storage energy of parent and N-substituted NBD/QC systems.

System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	96.06	1.04	121.76
IIa	56.47	0.61	144.93
IIIa	139.77	1.50	111.24
IVa	96.02	1.02	148.33
Va	13.48	0.14	175.38

Table S3: The storage energy of parent and N-substituted BND/TCN systems.

System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	222.00	1.85	64.18
IIa	210.76	1.74	72.64
IIIa	267.62	2.21	53.74
IVa	248.51	2.04	68.15
Va	196.29	1.61	75.26

Table S4: The storage energy of parent and N-substituted ABND/ATCN systems.

System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	220.32	1.82	56.55
IIa	207.42	1.70	66.21
IIIa	265.60	2.18	52.34
IVa	244.78	1.99	69.51
Va	191.19	1.55	76.90

Table S5: The storage energy of parent and N-substituted OBND/OTCN systems.

System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	213.25	1.75	71.83
IIa	201.42	1.64	84.02
IIIa	259.23	2.11	47.99
IVa	237.66	1.92	74.24
Va	183.37	1.48	71.98

Table S6: The storage energy of parent and N-substituted BDD/TCD systems.

System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	304.39	2.27	37.63
IIa	308.61	2.28	53.91
IIIa	345.65	2.56	-2.75
IVa	346.33	2.54	45.82
Va	299.63	2.20	66.52

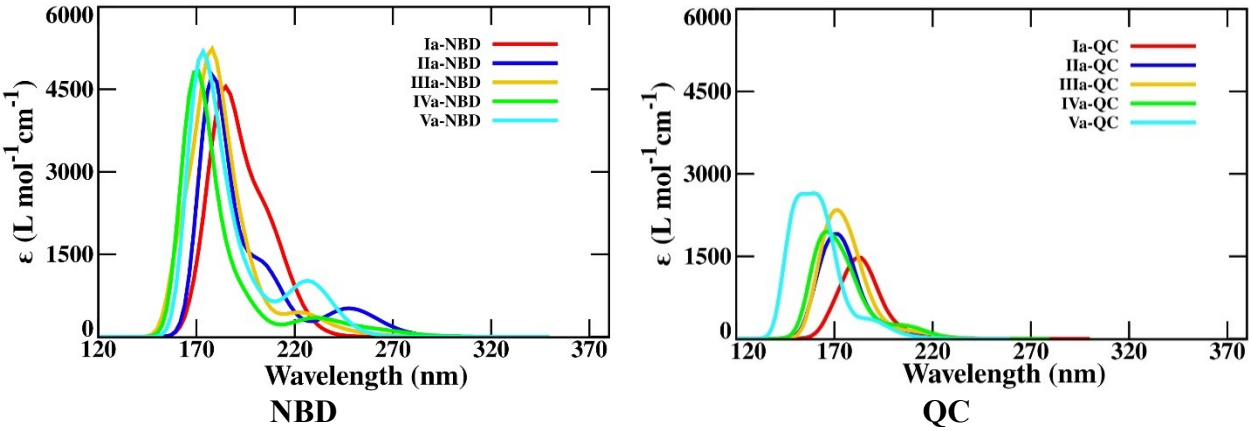
Table S7: The storage energy of parent and N-substituted ABDD/ATCD systems.

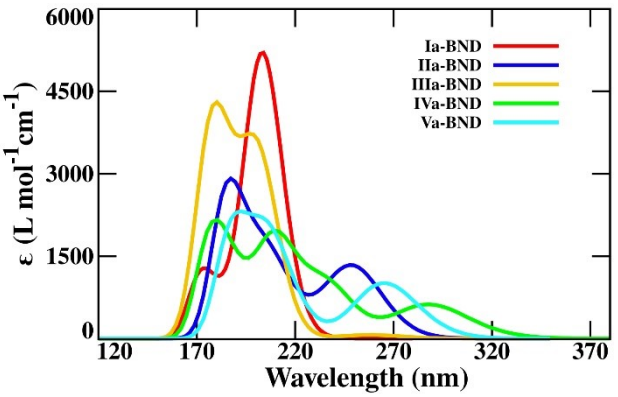
System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	299.99	2.22	38.27
IIa	301.08	2.21	59.32
IIb	304.61	2.24	47.06
IIIa	345.30	2.54	-2.04
IIIb	345.33	2.54	39.45
IVa	340.58	2.48	51.15
IVb	346.66	2.53	51.36
Va	292.52	2.13	56.56

Table S8: The storage energy of parent and N-substituted OBDD/OTCD systems.

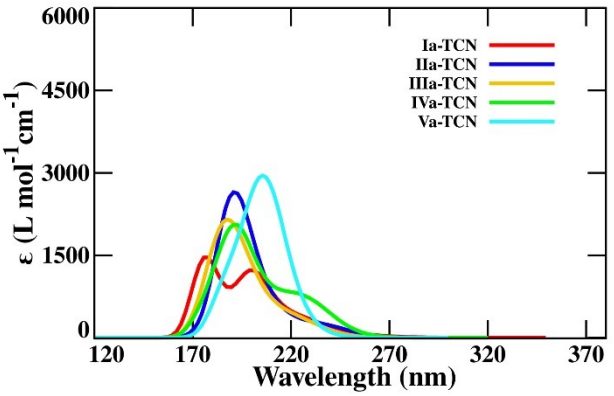
System	Storage Energy (kJ/mol)	Storage density	Back reaction Barrier (kJ/mol)
Ia	290.76	2.14	50.06
IIa	290.53	2.12	61.33
IIb	294.06	2.15	58.83
IIIa	342.35	2.50	42.95
IIIb	335.61	2.45	51.89
IVa	331.41	2.40	56.08
IVb	334.96	2.43	60.83
Va	280.37	2.03	60.49

S3: Photophysical properties

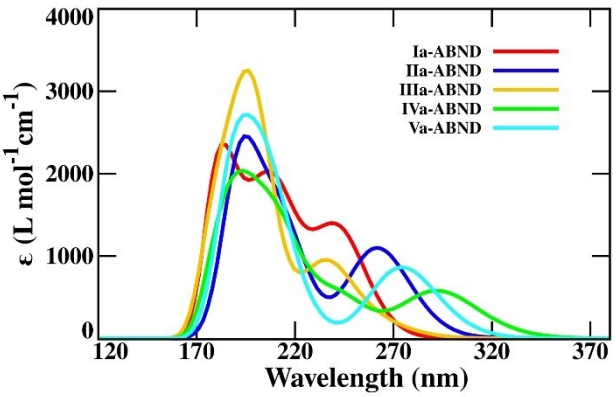




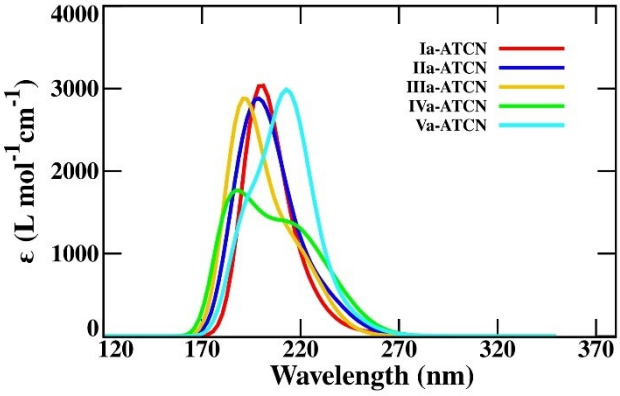
BND



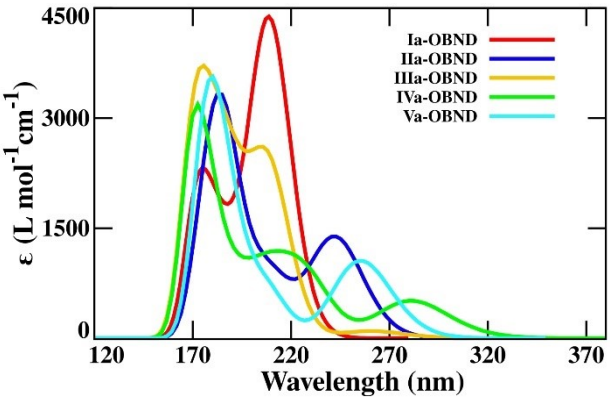
TCN



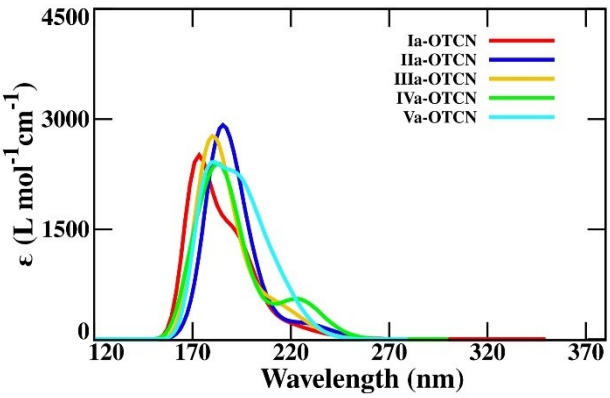
ABND



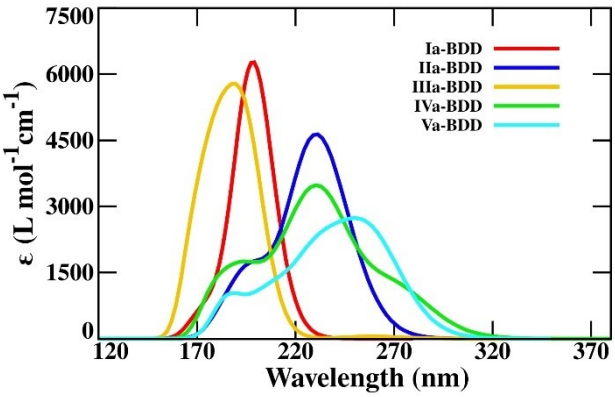
ATCN



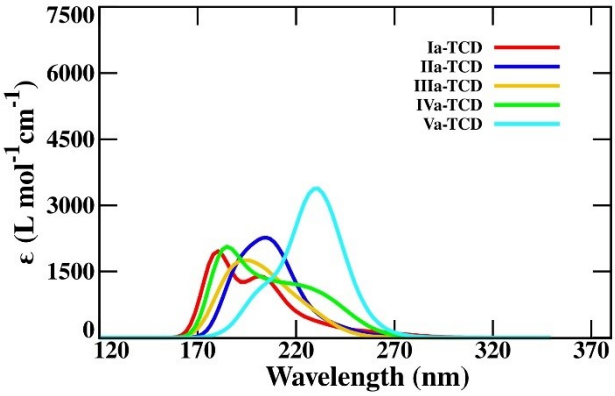
OBND



OTCN



BDD



TCD

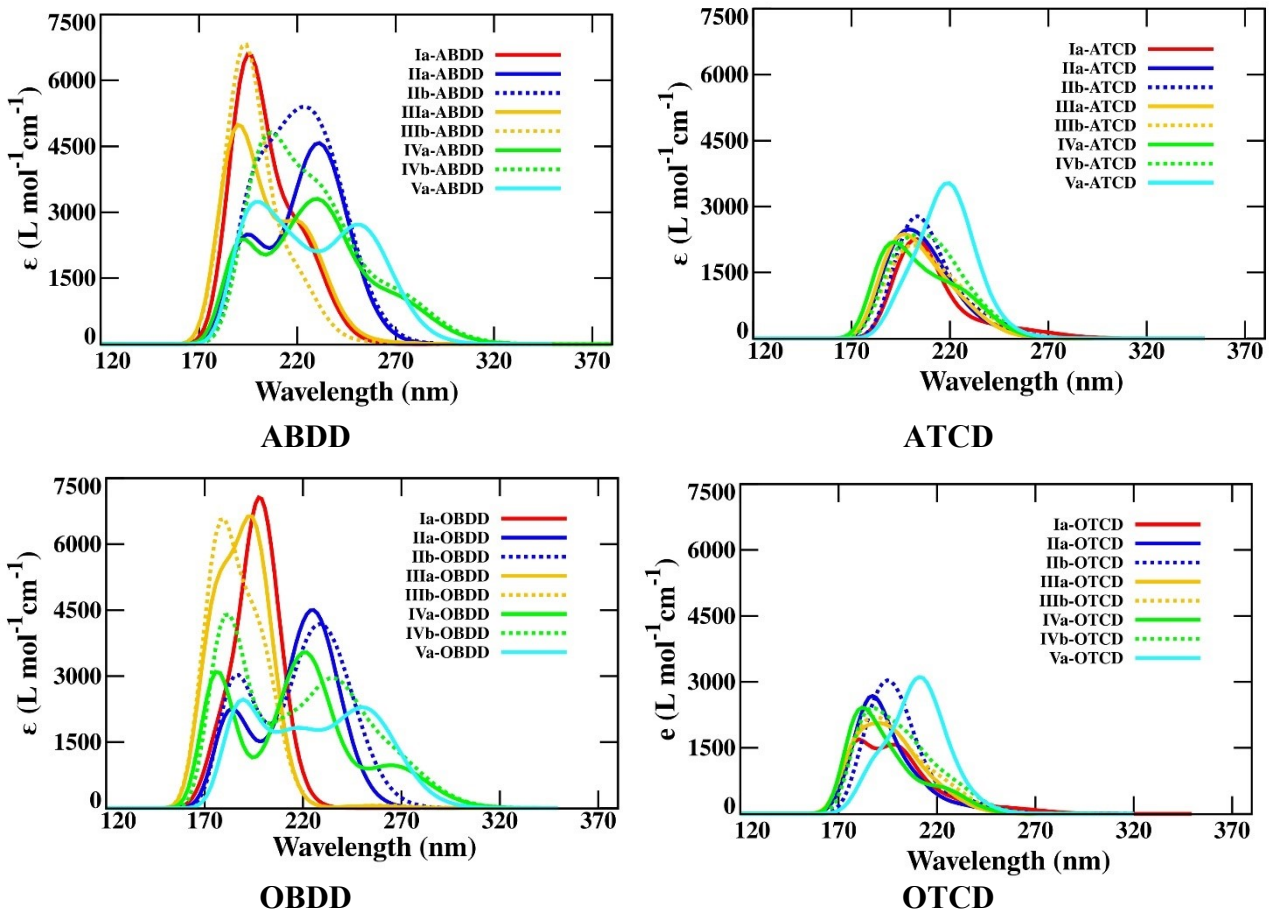


Figure S1. Optical absorption spectra of parent and N-substituted photoswitching systems.

Table S9: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the NBD/QC system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		**Product**	
Ia	214.42	0.0124	184.63	0.0149
IIa	247.90	0.0126	175.95	0.0126
IIIa	223.06	0.0104	171.19	0.0117
IVa	194.02	0.0126	177.11	0.0152
Va	227.04	0.0247	170.26	0.0108

Table S10: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the BND/TCN system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		Product	
Ia	206.69	0.0129	199.61	0.0190
IIa	249.45	0.0318	193.74	0.0202
IIIa	203.13	0.0593	196.60	0.0153
IVa	288.02	0.0153	229.64	0.0108
Va	265.36	0.0249	207.15	0.0606

Table S11: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the ABND/ATCN system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		Product	
Ia	242.09	0.0319	207.27	0.0141
IIa	261.94	0.0270	207.67	0.0157
IIIa	236.38	0.0209	223.11	0.0105
IVa	292.50	0.0142	219.79	0.0173
Va	274.38	0.0213	214.48	0.0612

Table S12: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the OBND/OTCN system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		Product	
Ia	213.22	0.0159	193.35	0.0162
IIa	242.44	0.0338	195.95	0.0166
IIIa	209.51	0.0525	190.24	0.0127
IVa	281.01	0.0126	186.95	0.0226
Va	255.32	0.0261	207.19	0.0150

Table S13: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the BDD/TCD system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		Product	
Ia	207.52	0.0165	202.19	0.0262
IIa	245.40	0.0211	207.74	0.0257
IIIa	196.41	0.0432	224.34	0.0101
IVa	271.66	0.0265	235.68	0.0115
Va	259.15	0.0491	230.68	0.0761

Table S14: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the ABDD/ATCD system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		Product	
Ia	223.66	0.0478	208.76	0.0102
IIa	239.74	0.0282	205.74	0.0108
IIb	243.22	0.0255	207.57	0.0302
IIIa	226.46	0.0202	212.69	0.0154
IIIb	218.97	0.0357	229.11	0.0121
IVa	270.45	0.0242	230.41	0.0107
IVb	271.44	0.0262	218.78	0.0158
Va	254.32	0.0561	222.32	0.0173

Table S15: The first important excitation wavelength with the oscillatory strength surpassing 0.01 for the OBDD/OTCD system calculated using M062X/6-311++G** level.

System	Absorption wavelength (nm)	Oscillatory strength	Absorption wavelength (nm)	Oscillatory strength
	Reactant		Product	
Ia	204.14	0.0248	198.98	0.0216
IIa	229.24	0.0552	191.76	0.0130
IIb	239.71	0.0391	200.92	0.0245
IIIa	199.16	0.0218	201.57	0.0154
IIIb	198.82	0.0688	200.17	0.0209
IVa	266.41	0.0233	198.68	0.0109
IVb	266.75	0.0251	228.66	0.0124
Va	254.89	0.0452	227.70	0.0105