Supporting Information

Protonation induced ultrafast torsional dynamics in 9-anthrylbenzimidazole : A pH activated molecular rotor

Amitabha Nandi[†], Archana Kushwaha[‡], Dipanwita Das[‡] and Rajib Ghosh[*,†],

[†]*Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India, E-mail:rajchem06@gmail.com*

[‡]*Department of Chemistry, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400019, India,*

Synthesis of 2-(anthracen-9-yl)-1H-benzo[d]imidazole (ANBI): Under nitrogen atmosphere, in a 50 mL round bottom flask, 1,2-phenyldiamine(450.9 mg, 4.17 mmol) and anthracene-9-carbaldehyde (860 mg, 4.17 mmol, 1eq.) were added in 15mL nitrobenzene for 18h. To the reaction mixture, 20 mL pet ether was added and filter. The residue was purified by column chromatography on silica (ethyl acetate/pet ether; 2:8 v/v) for the desired product. Yield: 78 % , ^{1}H NMR (400 MHz, d^6-dmso) :δ (ppm) = 12.99 (s, 1H), 8.81 (s, 1H), 8.19–8.17 (d, J = 8.4 Hz, 2H), 7.79–7.78 (d, J = 6.8 Hz, 1H), 7.66–7.63 (d, J = 8.6 Hz, 2H), 7.57–7.52 (dd, J = 13.2, 7.1 Hz, 3H), 7.50 – 7.46 (m, 2H), 7.31–7.25 (dd, J = 8.7, 6.0 Hz, 2H).

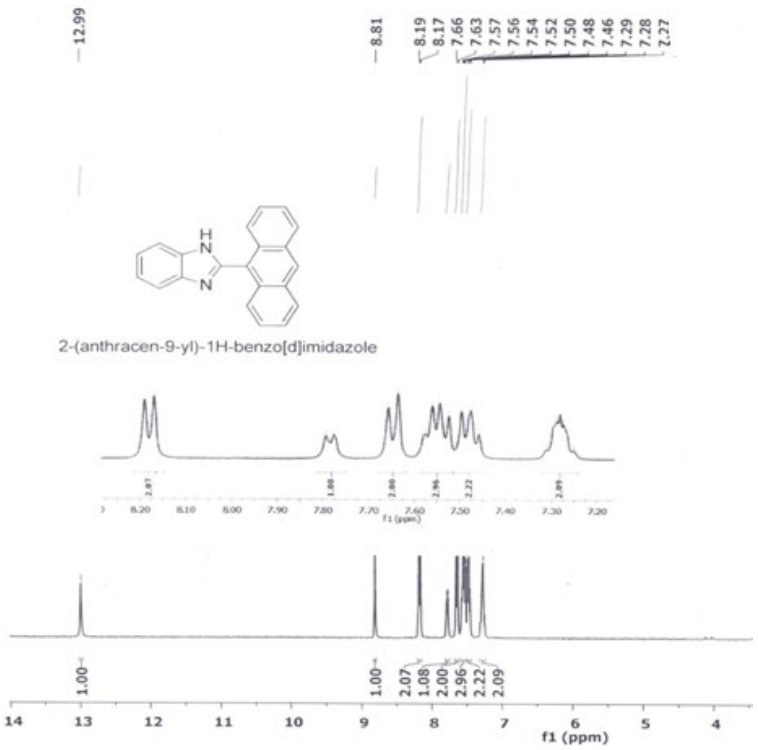

Figure S1: ^{1}H NMR spectrum of ANBI in deuterated DMSO.

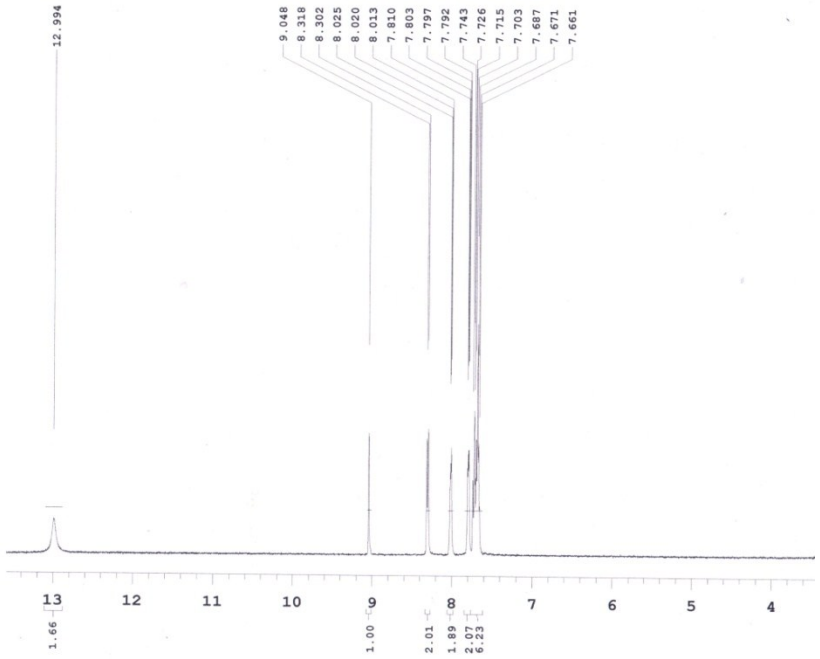

Figure S2: ^{1}H NMR spectrum of protonated ANBI cation in deuterated acetonitrile.

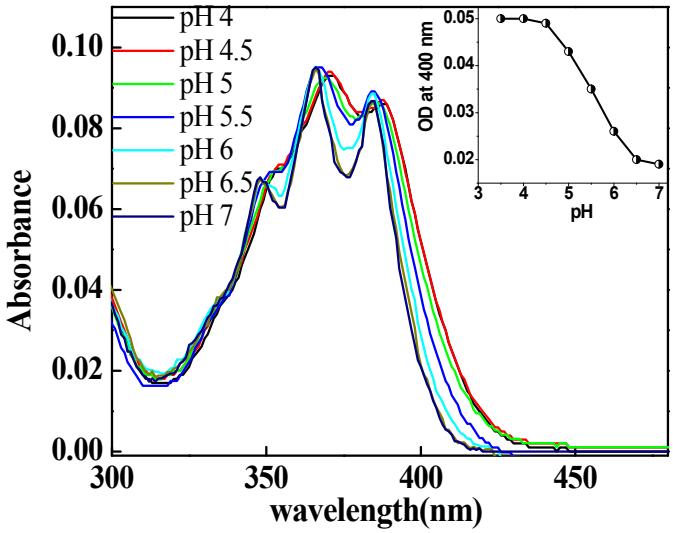

Figure S3: pH titration of ANBI in aqueous solution. Inset shows the change in OD at 400 nm as a function of pH. The pK_a of ANBI is determined to be about 5.5.

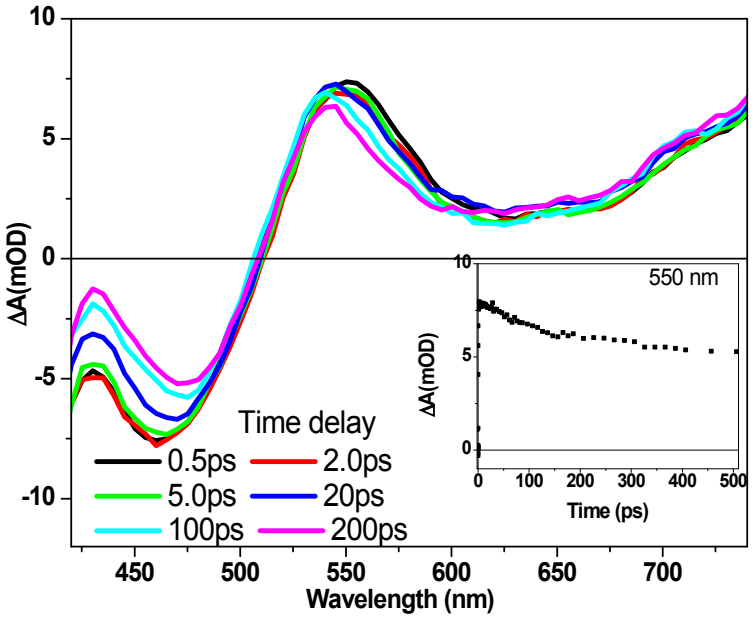

Figure S4: Transient absorption spectral evolution of protonated ANBI cation in glycerol following 390 nm femtosecond laser pulse excitation. Inset shows the decay trace of excited state absorption at 550 nm. Small red shift of stimulated emission band at 460 nm and blue shift of excited state absorption band in 550 nm in hundreds of picoseconds is due to slow solvation in glycerol.

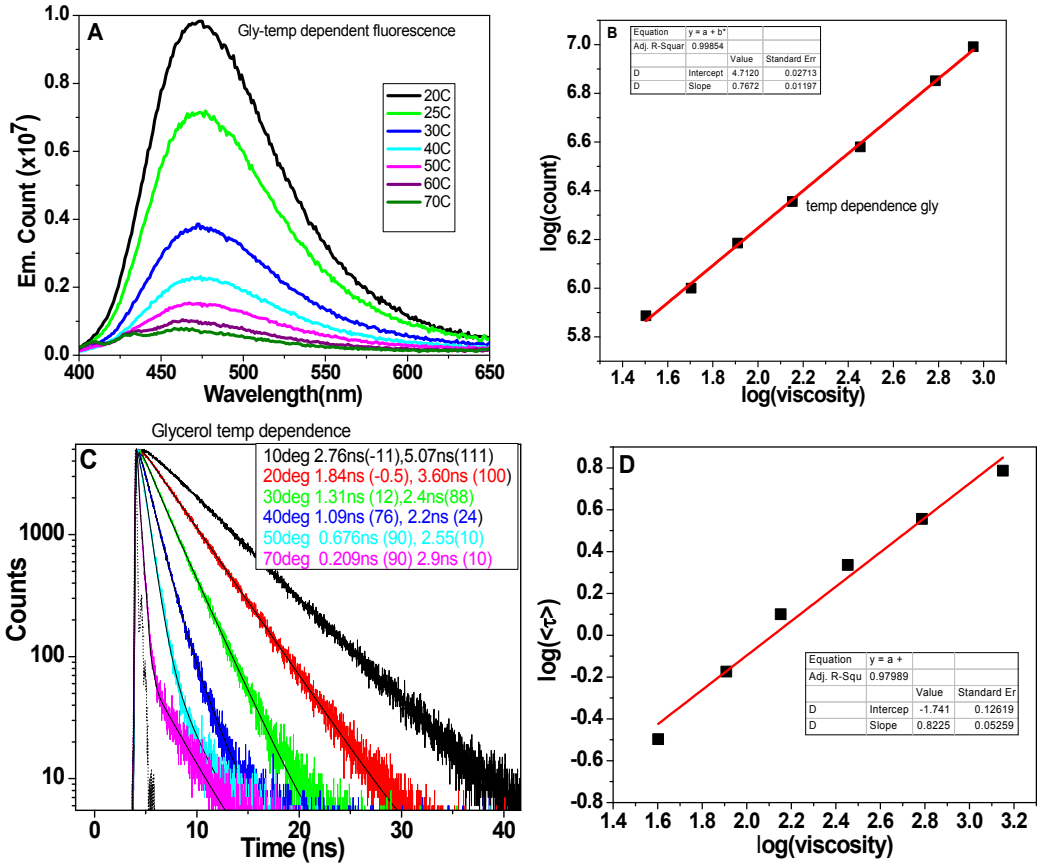

Figure S5: Variation of Emission intensity (A) and emission lifetime (C) with temperature of the glycerol solution of protonated ANBI cation. Log-log plot of emission intensity (B) and emission lifetime (D) versus viscosity of the glycerol solution changed upon temperature.

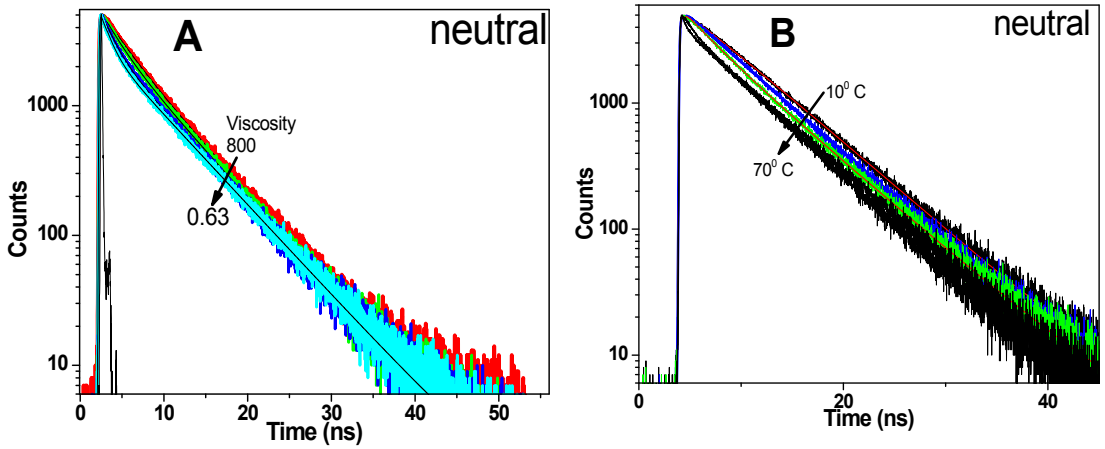

Figure S6: Viscosity dependent lifetime emission lifetime of neutral ANBI in the methanol-glycerol mixture (A) and in glycerol at different temperature (B).

Table S1: Atom coordinates of the ground state optimized structure of neutral ANBI.

C	-1.2946892083	-3.6683232173	-0.4317216596
C	-0.6384823169	-2.4691696196	-0.5088550505
C	-1.2842254742	-1.2292418678	-0.1822991978
C	-2.7073238749	-1.2966669176	0.0519262074
C	-3.3492704954	-2.5697605827	0.1549846706
C	-2.6597415598	-3.7305753463	-0.0440529727
C	-0.6203457654	0.0310314145	-0.1157404640
C	-3.4417989239	-0.1172170749	0.1549096637
C	-2.8312540733	1.1340684873	0.0783129246
C	-1.3917837069	1.2267435921	-0.0015922733
C	-0.8257817723	2.5411154609	0.0485379153
H	0.2468830048	2.6409469157	0.0038758497
C	-1.6172525036	3.6568627971	0.1021119650
C	-3.0335540594	3.5574560310	0.1141327932
C	-3.6199078610	2.3253508297	0.1131796211
H	-0.7712032291	-4.5821525478	-0.6907814410
H	0.3786710287	-2.4587056945	-0.8731948771
H	-4.4080046185	-2.5894340234	0.3925819194
H	-3.1530991433	-4.6908172377	0.0540344918
H	-4.5180446100	-0.1729213805	0.2874403890
H	-1.1525333819	4.6365452784	0.1297776629
H	-3.6401535291	4.4562302151	0.1311791720
H	-4.6999941572	2.2235566517	0.1345220840
H	6.2696207493	-1.0204926409	0.6077718540
C	5.3198200222	-0.5483962588	0.3830588057
C	5.3095281512	0.7469583561	-0.1702869829
C	4.1407620071	-1.2363916088	0.6439923037
C	4.1216368795	1.3800982836	-0.5081338728
H	6.2529690246	1.2547338979	-0.3362725276
C	2.9496557022	-0.5839634992	0.3235759974
H	4.1535756166	-2.2345688133	1.0668626636
C	2.9221456739	0.6963490044	-0.2742975121
H	4.1082743276	2.3747008746	-0.9375767944
C	0.8563852956	0.0869716923	-0.1023009586
H	1.2619811008	-1.7570615036	0.8985473407
N	1.6201226046	1.0728910782	-0.5328305905
N	1.6239207507	-0.9404019322	0.4342827741

Table S2: Atom coordinates of the S_1 state optimized structure of neutral ANBI.

C	-1.3496253496	-3.6793049134	-0.5913714312
C	-0.6788878075	-2.4458396019	-0.6536430469
C	-1.2783293926	-1.2472729968	-0.2199951460
C	-2.6643654594	-1.3117086276	0.1703855362
C	-3.3094466275	-2.5671937015	0.2458343162
C	-2.6560937374	-3.7439517540	-0.1190395195
C	-0.6034729009	0.0385879854	-0.1969231166
C	-3.3584257893	-0.1140476574	0.4189648315
C	-2.7808904622	1.1542531157	0.2265340610
C	-1.3860755117	1.2628342340	-0.1215567164
C	-0.8666240718	2.5541563362	-0.3207273235
H	0.1725791282	2.6573658647	-0.5938802593
C	-1.6657568271	3.6993462484	-0.1788951530
C	-3.0065428858	3.5918781385	0.1774634564
C	-3.5545831746	2.3276869654	0.3804057209
H	-0.8416139441	-4.5775670484	-0.9235689999
H	0.3118137053	-2.4219977424	-1.0878332246
H	-4.3409112202	-2.6000904809	0.5810779968
H	-3.1724915987	-4.6948457610	-0.0539693871
H	-4.4074450240	-0.1710164747	0.6951462816
H	-1.2221877364	4.6738467670	-0.3498176418
H	-3.6197840920	4.4779480382	0.2955314256
H	-4.5956962776	2.2240701992	0.6680935932
H	6.2121906945	-0.9982958208	0.8633724569
C	5.2759321533	-0.5440217676	0.5593535832
C	5.2972748703	0.7302631344	-0.0506800851
C	4.0860913701	-1.2304060522	0.7767804034
C	4.1314641409	1.3580149414	-0.4560522644
H	6.2514377779	1.2226501940	-0.2004647242
C	2.9132142615	-0.5990097346	0.3638164710
H	4.0782575567	-2.2083186793	1.2443165007
C	2.9134233768	0.6899234052	-0.2436048586
H	4.1397614342	2.3355863401	-0.9226334918
C	0.8380350964	0.0812186376	-0.1509478043
H	1.2035757616	-1.7790870700	0.8400516620
N	1.6388417318	1.0790153003	-0.5374746800
N	1.5928642678	-0.9624567952	0.3955853525

Table S3: Atom coordinates of the ground state optimized structure of protonated ANBI cation.

C	-1.4805582502	-3.6754676767	-0.3463910109
C	-0.7345642234	-2.5286469161	-0.2517510071
C	-1.3531564496	-1.2513038803	-0.0884645738
C	-2.7951255209	-1.2165414741	-0.1135267200
C	-3.5341167489	-2.4339961333	-0.2122975878
C	-2.8978573942	-3.6381713650	-0.3070908840
C	-0.6487928201	-0.0180638309	0.0490174406
C	-3.4554729748	0.0122412589	-0.0728566357
C	-2.7771950136	1.2259826412	0.0460652030
C	-1.3396765246	1.2261269709	0.1539501507
C	-0.7093989556	2.4815485884	0.4144517961
H	0.3532663112	2.5298437274	0.6130421492
C	-1.4346019430	3.6437601865	0.4750853311
C	-2.8407880703	3.6445809885	0.2885780383
C	-3.4927979601	2.4602460657	0.0965212149
H	-0.9782749295	-4.6284388204	-0.4673028517
H	0.3403218612	-2.6108607692	-0.3383448546
H	-4.6169966419	-2.3787135219	-0.2157293489
H	-3.4640634251	-4.5589021217	-0.3757662599
H	-4.5393400396	0.0229944944	-0.1307025212
H	-0.9260606518	4.5775011171	0.6865150601
H	-3.3889434319	4.5778822601	0.3263372279
H	-4.5715277746	2.4334932183	-0.0104257389
H	6.2894864576	-0.9244572354	0.7001932289
C	5.3327233800	-0.5224941889	0.3907748052
C	5.3045199700	0.5629995448	-0.5035475487
C	4.1666156821	-1.0925093705	0.8868331125
C	4.1086779454	1.1166446779	-0.9427347434
H	6.2397281317	0.9769620682	-0.8596505439
C	2.9679030460	-0.5339695094	0.4504772997
H	4.1933824090	-1.9281561149	1.5748621006
C	2.9403588281	0.5406660676	-0.4504736318
H	4.0889341562	1.9516544535	-1.6318499733
C	0.8068974613	-0.0143272979	0.0432899640
H	1.3048022930	-1.5175859286	1.3949245567
H	1.2235675807	1.5048394305	-1.3147899428
N	1.5930818540	0.8175057184	-0.6726277672
N	1.6335398240	-0.8334402394	0.7279537576

Table S4: Atom coordinates of the S_1 state optimized structure of protonated ANBI cation.

C	1.9008540198	-3.8760693238	0.1558942926
C	1.0312913622	-2.7953810016	0.1178185151
C	1.5168834321	-1.4630254858	0.0590717168
C	2.9460871392	-1.2710314236	0.0390394198
C	3.8044890613	-2.3945575080	0.0760969394
C	3.2893579447	-3.6805459255	0.1343770708
C	0.6432706976	-0.3415416493	0.0203561107
C	3.4671894079	0.0287814757	-0.0172334518
C	2.6273906935	1.1511093902	-0.0516560568
C	1.1986386334	0.9667542251	-0.0321745017
C	0.3846316218	2.1281056400	-0.0655218429
H	-0.6884502873	2.0253813776	-0.0504349936
C	0.9462829857	3.3956827675	-0.1156296000
C	2.3386932872	3.5653877046	-0.1359469538
C	3.1690286406	2.4567773784	-0.1045617332
H	1.5000923144	-4.8815224662	0.2016426155
H	-0.0357809055	-2.9596787337	0.1318605938
H	4.8770998433	-2.2368900919	0.0591050296
H	3.9584538167	-4.5318439594	0.1629020560
H	4.5430568292	0.1708949034	-0.0328316572
H	0.2995810995	4.2643839096	-0.1392319703
H	2.7639964755	4.5608323220	-0.1752460892
H	4.2459744442	2.5811906715	-0.1191795077
H	-6.1313923233	0.8689361846	-1.2739842440
C	-5.2161114161	0.6716490741	-0.7298171949
C	-5.2199748594	0.7258626628	0.6658340801
C	-4.0536645269	0.3608209149	-1.4411069121
C	-4.0617336940	0.4713135208	1.4058496836
H	-6.1383000762	0.9646734393	1.1877470866
C	-2.9007580108	0.1113234149	-0.7066436635
H	-4.0558438397	0.3109838577	-2.5232367443
C	-2.9045394656	0.1658817225	0.6997416281
H	-4.0704750569	0.5051690080	2.4885500926
C	-0.8458156824	-0.5852746007	0.0303108811
H	-1.4249490807	-0.6280667620	-2.0087371187
H	-1.4352090607	-0.4684871883	2.0636821222
N	-1.6107761651	-0.1216425711	1.1327373161
N	-1.6050436603	-0.2089877885	-1.1088833391

Table S5: DFT/TDDFT calculated excitation energies and dipole moment of ANBI in neutral and protonated state.

	$S_0 \rightarrow S_1$ Transition energies	Dipole moment of LE state	Dipole moment of TICT state
ANBI neutral	3.1 eV	4.1 D	-------
ANBI protonated	2.9 eV	0.9 D	7D

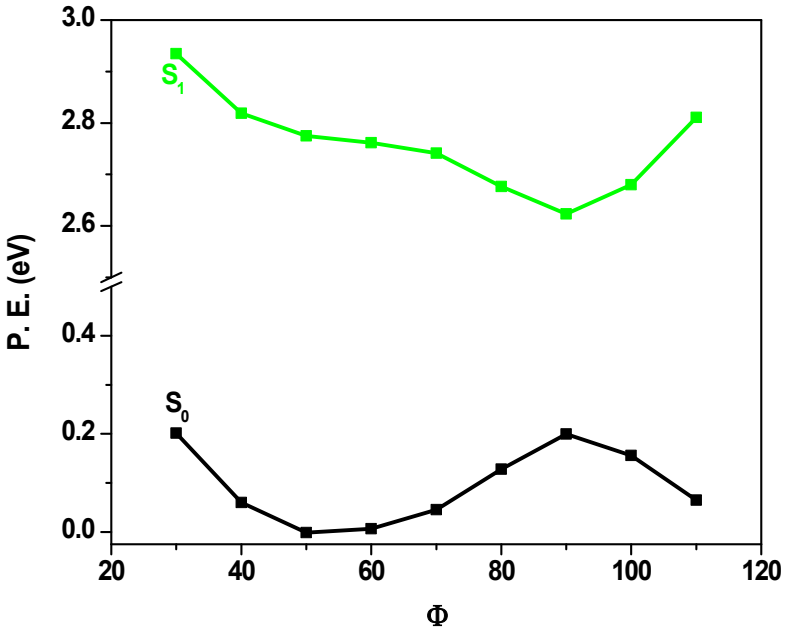

Figure S7: Calculated potential energy of protonated ANBI in S_0 and S_1 electronic states as a function of dihedral angle (Φ) between anthracene and benzimidazole groups.