Supporting Information

New zinc complexes derived from "self-adaptable" acyclic diiminodipyrromethanes as potent catalysts for the reduction of curing temperature of bisphenol-A/F benzoxazines

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Table 1: Crystallographic information of acyclic Schiff base (**2a**), zinc complexes (**3**) and (**4**).

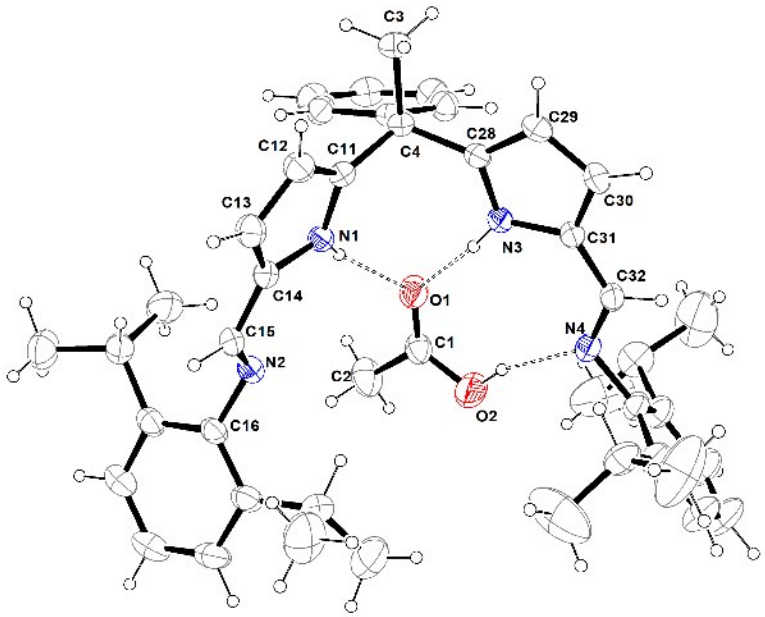


Figure S1: ORTEP diagram of acyclic diiminodipyrromethane Schiff base **2a** with thermal displacement parameters drawn at the 30% probability level. Selected bond lengths [Å] and bond angles[°]: C1–C2 1.484(4), C3–C4 1.543(3), C4–C11 1.513(3), C11–C12 1.369(3), C12–C13 1.394(4), C13–C14 1.364(4), C14–N1 1.369(3), C11–N1 1.364(3), C14–C15 1.439(4), C15–N2 1.264(3), C16–N2 1.424(3), C4–C28 1.515(3), C28–C29 1.377(3), C29–C30 1.392(4), C30–C31 1.373(3), C31–N3 1.370(3), C28–N3 1.359(3), C31–C32 1.419(3), C32–N4 1.271(3), C33–N4 1.435(3), C1–O1 1.199(3), C1–O2 1.299(4); O1–C1–O2 122.2(3), O1–C1–C2 123.5(3), O2–C1–C2 114.3(3), C11–C4–C28 109.72(19), C3–C4–C5 107.1(2), C3–C4–C11 108.7(2), C3–C4–C28 109.0(2), C4–C11–N1 122.6(2), C4–C28–N3 122.5(2), C11–N1–C14 110.2(2), N1–C14–C15 122.6(2), N1–C14–C13 106.7(2), C14–C15–N2 122.3(2), C15–N2–C16 119.8(2), C4–C28–N3 122.5(2), C4–C28–C29 130.4(2), C28–N3–C31 110.2(2), N3–C31–C32 125.9(2), C30–C31–C32 127.3(2), C31–C32–N4 127.6(2), C32–N4–C33 118.5(2).

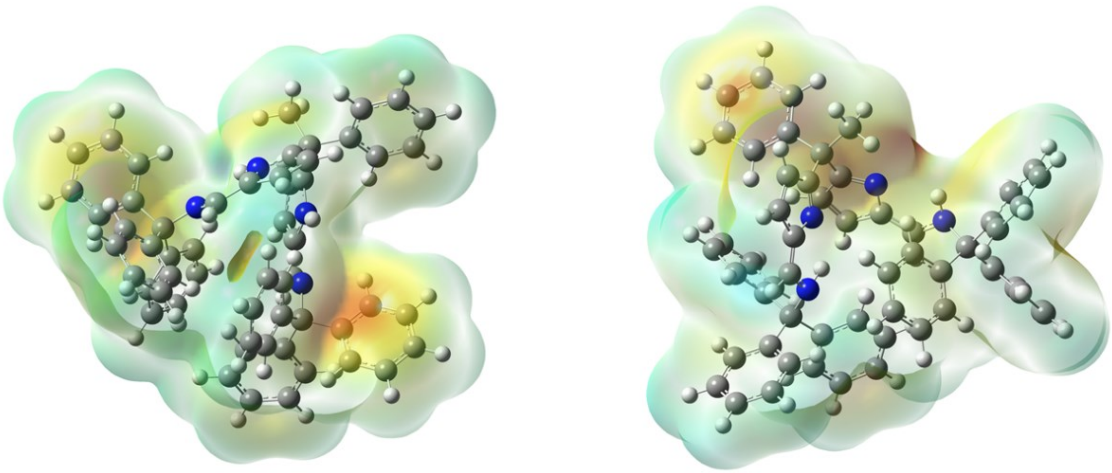


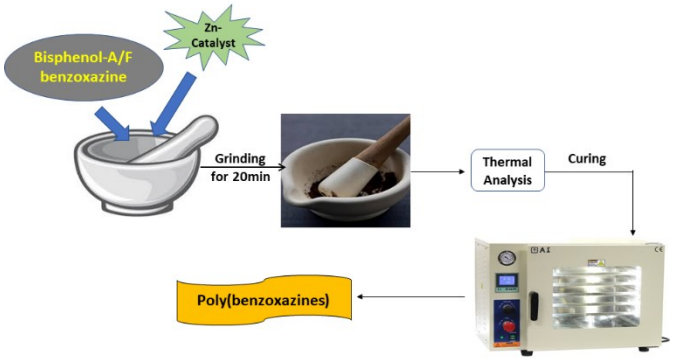
Figure-S2: ESP diagram of diiminodipyrromethane ligand **2b** and **2b-I**.

Typical procures for ROP of Benzoxazines:

Bisphenol-A (90 mg, 0.20 mmol) or Bisphenol-F (90 mg, 0.19 mmol) benzoxazine was mixed with 10% catalytic amount of Zinc complex **3 or 4** by physical grinding in a mortar with a pestle at room temperature for 20 min. to obtain a homogeneous mixture. After that 5.0 mg of the mixture was taken and placed in an aluminium pan and heated in the DSC instrument to obtain the corresponding heat evolution profile.

Curing process:

According to the DSC data , the remaining mixture was placed in a glass vial and it is introduced to time dependent temperature adjustable hydrothermal oven. Initially the oven temperature set it to be at room temperature gradually enhanced to its maximum curing temperature with respect to time. After 24 h we will get poly-benzoxazine as a product. The 5.0 mg of the resulted poly-benzoxazine was



placed in aluminium pan and heated in the DSC and TG instrument to study their heat evaluation profile and temperature-dependent weight loss and to see the improvement in residual char yield percentage.

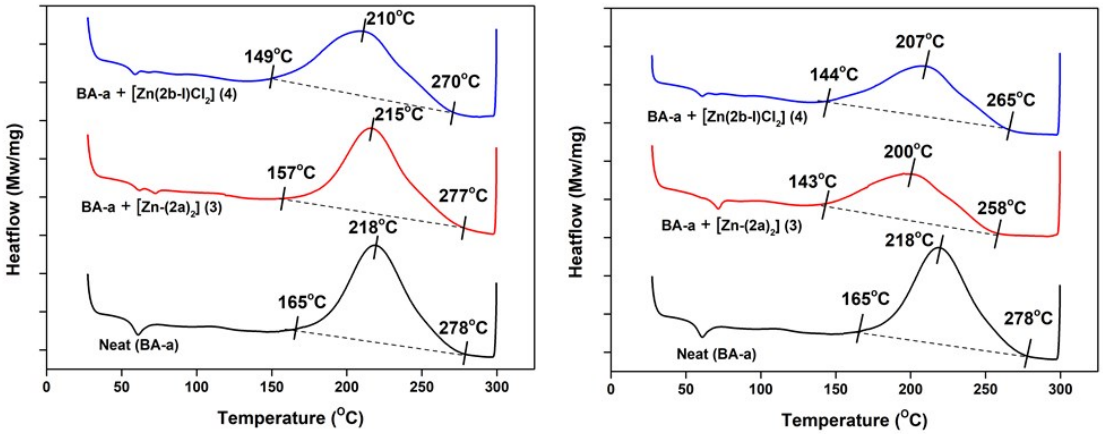


Figure-S3: DSC curing thermogram of BA-a benzoxazine with 3% (left) and 5% (right) zinc catalysts (**3** and **4**).

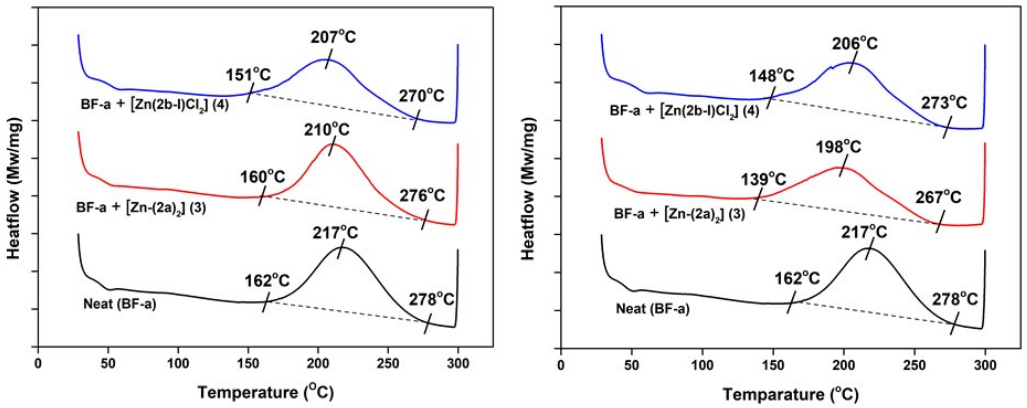


Figure-S4: DSC curing thermogram of BF-a benzoxazine with 3% (left) and 5% (right) zinc catalysts (**3** and **4**).

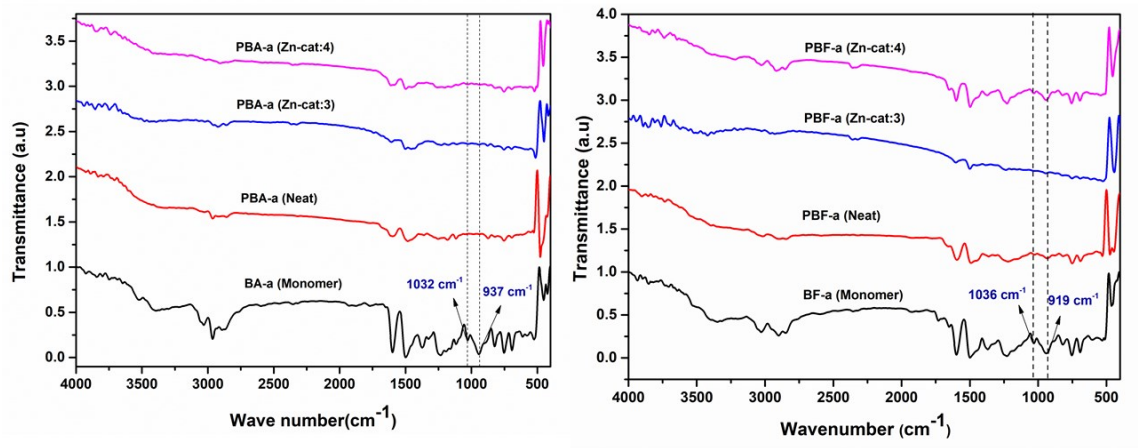


Figure-S5: IR-Spectra of benzoxazine monomers and PBz's with and without catalysts.

Table 1:

Crystal	**2a**	**3**	**4**
CCDC No.	1939817	1900503	1902678
Empirical formula	$C_{44}H_{54}N_4O_2$	C_{84} H_{98} N_8 Zn_1	C_{63} H_{54} N_4 Cl_2 Zn_1
Formula weight	669.90	1285.07	1003.46
T (K)	298(2)	298.15	298.15
λ (Å)	0.71073	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P* -1	*P* $2_1/c$	*P-1*
a (Å)	12.0275(7)	13.06630(10)	11.8769(3)
b (Å)	12.8465(6)	12.93910(10)	13.4192(4)
c (Å)	14.5982(8)	46.6200(5)	17.2498(4)
α (°)	104.022(4)	90	85.646(2)
β (°)	93.333(5)	98.0010(10)	89.156(2)
γ (°)	108.901(4)	90	73.944(3)
V (Å^3)	2047.3(2)	7805.14(12)	2634.32(13)
Z	2	4	2
D_{calc} g cm^{-3}	1.087	1.094	1.2650
μ (mm^{-1})	0.067	0.784	1.911
F (000)	722.0	2752.0	1048.9
Theta range for data collection	4.292 to 58.354 deg.	6.832 to 148.74 deg.	8.28 to 148.94 deg.
Limiting indices	-15<=h<=15 16<=k<=16, -18<=l<=19	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -47 ≤ l ≤ 58	-11 ≤ h ≤ 14, -13 ≤ k ≤ 16, -20 ≤ l ≤ 21
Reflections collected / unique	15950 / 9346 [R(int) = 0.0270]	88203 [R(int) = 0.0386]	26749 [R(int) = 0.0283]
Completeness to theta = 74.37	99.3 %	88.1 %	95.4 %
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9346 / 0 / 463	14046 / 0 / 826	10280 / 0 / 680
Goodness-of-fit on F^2	1.042	1.004	1.041
Final R indices [I>2sigma(I)]	R_1 = 0.0744, wR_2 = 0.1677	R_1 = 0.0553, wR_2 = 0.1332	R_1 = 0.0576, wR_2 = 0.1512
R indices (all data)	R_1 = 0.1384, wR_2 = 0.2128	R_1 = 0.0585, wR_2 = 0.1361	R_1 = 0.0642, wR_2 = 0.1560
Largest diff. peak and hole	0.33 and -0.18 e.A^-3	1.29 and -0.74 e.A^{-3}	1.29 and -0.87 e.A^{-3}

Crystallographic information of acyclic Schiff base (**2a**), zinc complexes (**3**) and (**4**).